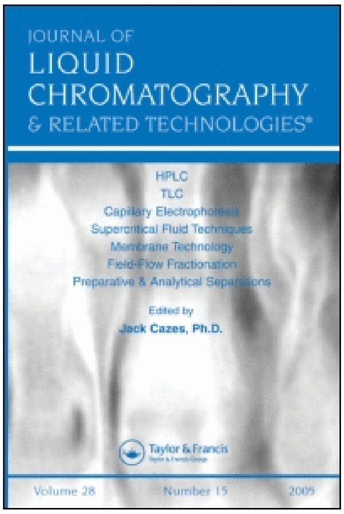


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

The Magic Square. The Usage of Double Bonds Photoisomerization for Identification of Organic Compounds by Thin-Layer Chromatography. II. Identification of Substances Forming Isomerizing Derivatives

B. K. Kerzhner[a]; V. I. Kofanov[a]; T. L. Vrubel[a]
[a] A. V. Dumansky Institute of Colloid and Water Chemistry Ukrainian Academy of Sciences, Kiev, USSR

To cite this Article Kerzhner, B. K. , Kofanov, V. I. and Vrubel, T. L.(1988) 'The Magic Square. The Usage of Double Bonds Photoisomerization for Identification of Organic Compounds by Thin-Layer Chromatography. II. Identification of Substances Forming Isomerizing Derivatives', Journal of Liquid Chromatography & Related Technologies, 11: 15, 3091 — 3102

To link to this Article: DOI: 10.1080/01483918808076782

URL: http://dx.doi.org/10.1080/01483918808076782

JOURNAL OF LIQUID CHROMATOGRAPHY, 11(15), 3091-3102 (1988)

THE MAGIC SQUARE. THE USAGE OF DOUBLE BONDS PHOTOISOMERIZATION FOR IDENTIFICATION OF ORGANIC COMPOUNDS BY THIN-LAYER CHROMATOGRAPHY.

II. IDENTIFICATION OF SUBSTANCES FORMING ISOMERIZING DERIVATIVES

B.K. KERZHNER, V.I. KOFANOV AND T.L. VRUBEL
A.V. Dumansky Institute of Colloid and Water Chemistry
Ukrainian Academy of Sciences
Kiev, USSR

ABSTRACT

The methods for derivatization of phenols, substituted aromatic aldehydes, ketones and amines to produce substances containing $-N{=}N-$, $>C{=}C<$ and $>C{=}N-$ bonds have been considered. The latter are capable to form a four - spot square as a result of two-dimensional chromatography with preliminary UV-irradiation before each development. It is shown, that on the sorbent layer take place reversible Z - E, syn - anti and azomethine-methanolamine conversions, which permit to obtain the magic square on TLC plates and thus to identify organic compounds in complex mixtures.

INTRODUCTION

In previous papers we have described the simple method for identification of double bond-containing organic substances in TlC (1,2). It includes two-staged UV-irradiation with interstitial chromatography and final development of the plate in the orthogonal direction (3). The spots of those compounds, which are able to form stable Z- and E-isomers on the sorbents surface are disposed in the squares verfices but other compounds extend along the straight line, passing through the start- and cross-points of the eluent fronts. Thus, during the analysis, the separation of the products present in the sample and the determination of reversably izomerizing compounds can be achieved. Due to the sorbent action one succeeds to obtain the magic square for some compounds forming sterically hindered Z-isomers (and so instable or not existing in a solution) (4,5).

It was interesting to investigate the possibilities of the magic square in identifying compounds which are capable to produce double-bonded derivates. The present work deals with the investigations of compounds containing -N=N-, $>C=C<$ and $>C=N-$ bonds prepared by the condensation or combining. Our attention was mainly attracted by the reactions of chromophoric groups introduction, developed in the frame of the photometric analysis applied to different classes of organic compounds (6).

EXPERIMENTAL

The introduction of azo-substituents into phenols and anilines was carried out by the azo-combination reaction with $PhN_2^+BF_4^-$. Add 0,5 ml of pure aniline to 4,0 ml HBF_4 dropwise while stirring. Cool obtained precipitate on the ice bath and add solution of 0,4 g $NaNO_2$ in 1,5 ml of water by drops while stirring. Precipitate of $PhN_2^+ BF_4^-$ suck and dry on the glass porous filter. Azo-combination with substituted anilines, naphthylamines, phenols and naphtols carry out as usually (6). Neutralize the reaction mixture and the dyes formed extract into chloroform.

The derivatization of free hydroxy- and amino- groups was performed by acylating mixture (boron trifluoride solution in acetic anhydride) according to (7).

Mix an extract and acylating mixture in equal volumes for 15 min at a room temperature in the concentrator (a pear-shaped flask with forged out tip). Dilute the reaction mixture by the three-fold volume of a saturated aqueous solution NH_4F. Acylated products are transfered to a deposited chloroform layer.

The introduction of an ethylene-substituents was carried out by the condensation of aldehydes with acetone leading to chalcones.

Place into concentrator 10-20 mg of aldehyde add 1,0 ml of acetone, 1,0 ml of the 60% aqueous solution of H_2SO_4 or 9 N KOH solution. Reflux the reaction mixture for 20 min on a water bath. Cool to the room temperature and dilute with water to volume 20 ml, neutralize and extract using benzene.

To produce chalcone from benzaldehyde, an acid was used while to synthetize it from furfurol an alkali was taken.

The introduction of azomethine group into aromatic aldehydes was performed by condensation as described in (6).

Place 10-15 mg of aldehyde into the concentrator, add 20 mg of $NH_2OH \cdot H_2SO_4$ dissolved in 1,5-2,0 ml of ethanol and 1,0-1,5 ml of an aqueous solution containing 30 mg NaOH. Reflux 2-3 min on the water bath. Cool, dilute with 20 ml of water, acidify up to pH=1 and extract aldoximes using diethyl ether.

Ketoximes of substituted benzophenones are similarly obtained; heating time is to be increased up to 40 min.

Azomethine derivatives having Shiff's bases structure were obtained by condensation of substituted anilines with aromatic aldehydes.

Mix in equimolecular quantaties 5-10 mg of aniline and aldehyde dissolved in 2 ml of ethanol, add 1 drop of concentrated HCI, heat gently for 5 min, cool, dilute to 5-fold volume by water, neutralize with ammonia and extract using diethyl ether. (Because these reactions are reversible, initial compounds and final products were chromatographicaly observed usually).

The chromatography of the obtained azo-, ethylene- and azomethine derivatives was performed on silica gel TLC plates (Merck N 5721 in the most cases). Before each case of the chromatography the irradiation was carried out using the UV-lamp (HP, 0,5 kWt) placed at a distance of 20 cm from the layer for 2-5 min. The irradiation time should be experimentally established for every specific case in order to minimalize any possible resinification of the spots.

The chromatography was performed within a chamber with saturation and eluting hexane-acetone mixture. The mixture composition is chosen depending on the type of mixtures to be separated.

RESULTS AND DISCUSSION

While analysing complex mixtures of organic compounds in coloured media, for example in waste water, often the necessity to check that particular compound is found correctly, that is in an additional identification method occurs. When applying the TLC in addition to the R_f value the magic square method can be used to this purpose.

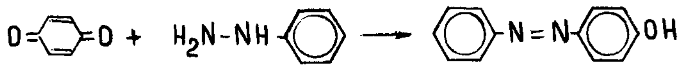
The magic square for azocompounds. The identification of aromatic compounds, substituted by amino- or oxy-groups can be additionally confirmed by magic square after reaction with diazonium salt. This results in the formation of azo-compounds:

$$ArN_2^+X^- + Ar'OH \rightarrow Ar-N=N-Ar'OH$$
$$ArN_2^+X^- + Ar'NH_2 \rightarrow Ar-N=N-Ar'NH_2$$

Azo-dyes containing free amino- and hydroxygroups conjugated with azogroup in their molecules do not form stable Z-isomers neither in a solution nor on a surface after the irradiation. The quinonhydrazone tautomerism and the vibrational deactivation of exited molecules prevent the isomerization. We could not succeed to chromatographically establish the isomerization in any of the investigated azo-dyes containing free amino- and hydroxy-groups in the adsorbed state. The acylation of free functional groups, however, did permit to obtain reversibly isomerizing azo-compound derivatives. Also, the alkylation with diazomethane leads to receiving of the magic square in oxyazocompounds. The obtained R_f values for the Z- and E- izomers of aromatic amines and hydroxy-compounds derivatives are given in Table 1.

In addition, for aminocompounds the reaction of oxidation with ozone in a corresponding nitroazocompound which also gave the magic square (4), proved to be suitable. Also other oxidation methods can be used to receive the magic square. These oxidation methods serve for the oxidation of phenols to obtain quinones and for that of anilines to produce nitrozocompouns. The obtained products can be rather easily condensed with the formation of azo-dyes which either lead to the magic square in their resulted form, or require the acylation of a free hydroxygroup, i.e.:

$$ArNO + H_2NOH \longrightarrow Ar\text{-}N{=}N\text{-}OH \xrightarrow{Ar'OH} Ar\text{-}N{=}N\text{-}Ar'OH$$



<u>The magic square for ethylene derivatives</u>. The production of olefinic compounds has a more restrictive significance for the organic analisys, as their synthesis under "test tube conditions" is impeded. Besides, numerous reactions of aldehyde condensation with the compounds having active methyl group in their composition are the most attractive.

$$PhCHO + (CH_3)_2CO \longrightarrow Ph\text{-}CH{=}CH\text{-}CO\text{-}CH_3$$

We have used the above reaction to determine benzaldehyde and furfurol through their derivatives, the chalcones. For the product of the benzaldehyde and acetone condensa-

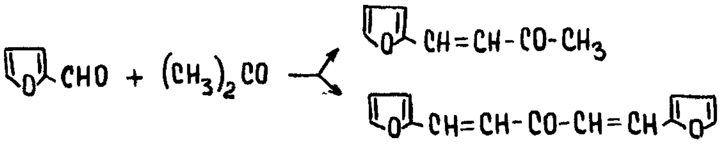
Table 1

Chromatographic mobility of azoderivatives of aromatic amines and alcohols while obtaining magic square

Identified compound	Derivative with azogroup	Derivatization of free functional groups	R_f isomers values Z isomer	 E isomer
Aniline	4-aminoazobenzene	$NHCOCH_3$	0,43	0,60
2-Naphtylamine	1-phenylazo-2-naphtylamine	$NHCOCH_3$	0,50	0,81
Phenol	4-oxyazobenzene	OCH_3	0,31	0,74
Phenol	4-oxyazobenzene	$OCOCH_3$	0,53	0,72

tion the R_f values of the Z- and E- izomers in the hexane - acetone eluent (2:1) were 0,32 and 0,44 respectively.

The form of chromatograms will depend on the type of a reagent. Thus, for acetone the condensation of both methyl groups resulting in the production of both symmetric and asymmetric chalcones is possible. The reaction of acetone with furfurol proceeds as follows:



Indeed, one can observe two overlapping squares on the chromatograms. The R_f values for both isomers of yellow-coloured symmetric chalcone are 0,39 and 0,49 respectively and the absorbtion in the UV-spot region at R_f equal to 0,43 and 0,53 are related to an asymmetic derivative.

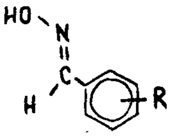
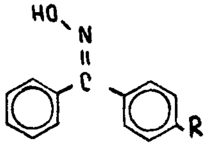
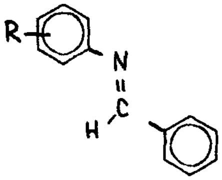
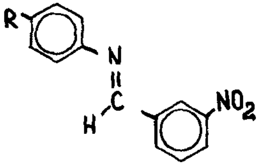
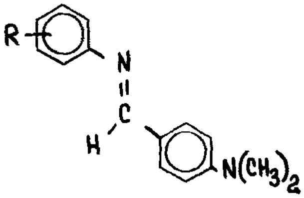
The magic square for azomethine derivatives. A wider range of substances can be identified after the introduction of azomethine group what is associated with the existence of numerous methods for the production of appropriate derivatives for different classes of organic compounds. This paper deals only with azomethine derivatives of aromatic aldehydes, ketones, and amines (oximes and Shiff's bases), though from the published data one can expect the magic square formation for other reversively isomerizing compounds with $>C=N-$ bond, for example, hydrazones, etc.

Table 2 gives R_f values for substituted benzaloximes. As it could be expected, the change of molecule geometry does not significantly affect the chromatographic mobility. As it is seen from the R_f values given in Table 2, the maximum difference does not exceed 0,1. Probably for this reason the use of hydroxylated sorbents does not permit the separation of the syn- and anti- isomers in the investigated ketoximes what however, gives the possibility to differentially determine the substituted aromatic aldehydes and ketones by applying the magic square method to their azomethine derivatives.

In principle, the aromatic azomethine(Shiff's bases) formation can be used for cross determination of aromatic aldehydes and amines in one stage. A lower activation

Table 2

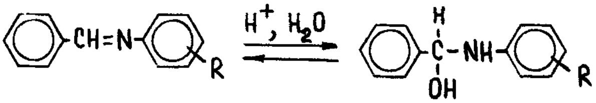
Chromatographic mobility of aromatic aldehydes, ketones, and amines while obtaining magic square

Identified compound	Derivative with azomethine group	R_f-values of: Z isomer	E isomer
Benzaldehyde		0,30	0,39
p-Brombenzaldehyde		0,27	0,36
p-Chlorbenzaldehyde		0,26	0,35
m-Nitrobenzaldehyde		0,17	0,22
p-Methylbenzophenon		-	0,24
p-Chlorobenzophenon		-	0,27
p-Dimethylamino-benzophenon		-	0,15
		methanolamine	azomethine
p-Toluidine		0,43	0,60
2,4,6-trimethyl-aniline		0,55	0,76
Aniline		0,41	0,47
p-Toluidine		0,43	0,60
p-Bromaniline		0,42	0,50
Aniline		0,55	0,69
m-Toluidine		0,55	0,70
p-Bromaniline		0,65	0,82
p-Nitroaniline		0,52	0,56
3,4-Dichloraniline		0,61	0,80

energy of isomer transformations of $>C=N-$ bond in Shiff's bases stipulates their existence in the form of an equilibrium mixture of syn- and anti- modifications under normal conditions. For the simplest representative of a given row, benzalaniline, we observed the hydrolysis on silica gel surface during the irradiation. Apart aniline and benzaldehyde any other products of photoreaction were not discovered. As the observed transformation can be classified as the photohydrolysis reactions (the excitation of a molecule is accompanied by theincrease of nitrogen atom basicity), it is reasonable to suppose that the introduction of acceptor substituent conjugated with a bridge group, as it follows from the consideration of electron structure of Shiff's bases, will lead to the increase of their molecules stability under the photoirradiation. In fact, having conducted the condensation of m-nitrobenzaldehyde with substituted amines given in Table 2, we succeeded to obtain the derivatives determined by the magic square method. It is interesting that the use of the p-dimethylaminobenzaldehyde also leads to a positive result in spite of apparent contradictions with the above statement. It is reasonable to suppose that in this case the $-N(CH_3)_2$ subtituent looses its donor properties due to the interaction with acid centres of the silica gel surface and the formation of cation-like

$$-\overset{\delta+}{N}(CH_3)_2 \; \ldots \; H-\overset{\delta-}{O}-Si-$$

It should be noted that for Shiff's bases given in Table 2 magic square probably result in another mechanism than syn- anti- isomerisation. We consider that the reverse hydratation of the azomethine group into a substituted methanolamine one on acid centres of the hydrated silica gel surface takes place according to the following scheme:



To justify this assumption several Shiff's bases produced from the p-dimethylaminobenzaldehyde were examinated. Two spots, upper yellow and lower colourless can be observed on chromatograms after a short exposure even without UV-irradiation before the chromatography. Several minutes later the colouring of the upper spot decreases and the turning but of the lower spot to yellow takes place. The magic square shows the establishment of an equilibrium on the layer. Certainly such colour changes and R_f values testify not so much the occurence of the molecule geometry changes (isomerization) as that of the break of conjugated electrone system results in azomethine group hydratation, but still this is a phenomenon of the reverse reaction occuring on the layer.

CONCLUSION

It is shown, that derivatization of the substituted aromatic compounds permits to identify them by the magic square method. Azo-, ethylene- and azomethine derivatives of phenols, anilines, aromatic aldehydes, ketones and acetone were studied. Summing up the obtained results leads to a conclusion that the identification of a wide range of organic compounds by the magic square is possible provided that the methods for their unsaturated derivatives preparation are available.

REFERENCES

1. Kerzhner B.K., Vrubel T.L., Kofanov V.I. Khimiya i tekhnologiya vodi, 4 (2), 151, 1982.
2. Kofanov V.I., Kerzhner B.K., Vrubel T.L. J.Liq.Chromatogr., 8 (7), 1239, 1985.
3. Kerzhner B.K., Vrubel T.L. Proc.III Intern.Symp.Instrumental Thin-Layer Chromatogr. Würzburg, 1985. Published by Inst. for Chromatography. Bad Dürkheim.W.Germany.P.93.
4. Kerzhner B.K., Kofanov V.I., Vrubel T.L Zhurnal Obshchei Khimiyi 53 (10), 2303, 1983.
5. Kerzhner B.K., Vrubel T.L., Kofanov V.I. Zhurnal Obshchei Khimiyi 57 (5), 1172, 1987.
6. Korenman I.M. Metodi opredeleniya organicheskikh soyedineniy. Khimiya.M.1970, 343 s.
7. Nevinnaya L.V., Kofanov V.I. Khimiya i tekhnologiya vodi, 6 (4), 326, 1984.