

## Determination of side products of stilbene synthesis by gas chromatography and chromato-mass spectrometry

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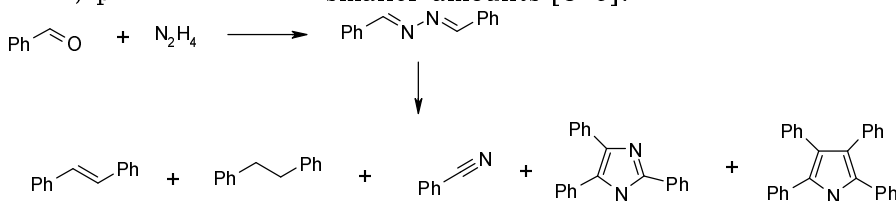
The impurity composition of *trans*-stilbene obtained by synthesis and purified by various techniques has been studied using combination of gas chromatography and chromato-mass-spectrometry. The results obtained made it possible to identify the impurities to be limited and to improve the technology of scintillation grade *trans*-stilbene.

С помощью комбинации методов газовой хроматографии и хромато-масс-спектрометрии исследован примесный состав *транс*-стильбена, получаемого синтетическим путем и очищенного различными способами. Полученные результаты позволили идентифицировать лимитируемые примеси и уточнить технологию получения сцинтилляционного *транс*-стильбена.

For the fast neutron spectrometry, media with a high hydrogen content are necessary that are capable of radioluminescence and providing the separation of the neutron flux signals from the background gamma radiation. Those requirements are met by organic liquid and crystalline scintillators. Liquid scintillators are difficult to use in many cases for practical reasons. The *trans*-stilbene crystals are the best known scintillators for spectrometry of mixed ionizing radiation fluxes, including those of high-energy neutrons [1]. That application of stilbene imposes very stringent requirements to its quality. To optimize the purification technology, it is necessary to know the impurity composition of the initial synthetic stilbene. In this work, presented are results of a comparative study of *trans*-stilbene samples obtained from various sources and purified by a complex procedure.

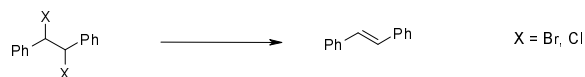
First, let the stilbene synthesis methods

be reviewed briefly. Only the methods suitable for large-scale synthesis will be taken into consideration which provide a high product yield (at least 75 %) and/or make use of easily available and relatively cheap initial reagents. The review data will be used in the frame of this work to substantiate the selection of components for model mixes. One of the practical methods is based on the work by Meisenheimer and Heim [2] who have shown that benzalazine is decomposed at 325°C with stilbene formation and nitrogen release. Later, it was stated that the benzalazine pyrolysis gives benzonitrile, ammonia, diphenylethane, a series of polyarylsubstituted heterocycles in comparable amounts as well as phenantrene in smaller amounts [3-6].



Stilbene yields in that method are relatively low and attain 20 or 25 % only, although there is a report [6] on the stilbene content up to 60 %, as determined by gas chromatography.

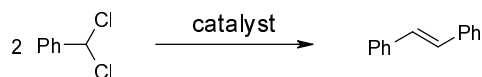
Stilbene can be obtained also by reductive dehydrohalogenation of 1.2-dihalo-1.2-diphenylethane.



Along with traditional reduction techniques (e.g., using sodium borohydride with 96 % yield [7]; iron, 90 % [8]; hydrogen, 70 % [9]), microwave activation can be used successfully to obtain the required product at an essentially quantitative yield, see, e.g. [10].

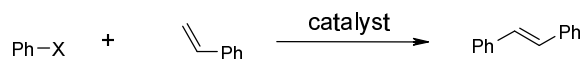
In [11], stilbene has been obtained by electrochemical reduction of benzaldehyde in acidic medium. The product yield was as low as 10 %. Later, the same method has provided the stilbene yield over 95 % using low-valence titanium [12] or chrome [13] reagents.

The cross-combination reactions catalyzed by transition metals constitute a separate group of stilbene synthesis methods. For example, stilbene can be obtained at yields exceeding 80 % using 1.1-dichlorotoluene as the initial material:



Catalyst	Stilbene yield, %	Ref.
(Cod) <sub>2</sub> Ni	96	14
ZrCl <sub>2</sub>	99	15
(Et <sub>3</sub> P) <sub>4</sub> Ni	98	16
Iron oxalate	92	17

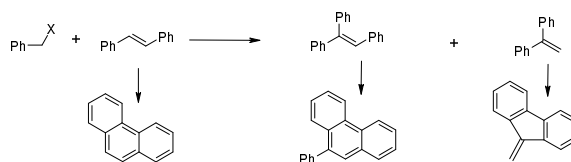
A more prospective way is to arylate styrene with halobenzenes (the Hack-Mizokori reaction, see, e.g., review [18]). Even for the least reactive halide, chlorobenzene, conditions are reported providing the product yield over 90 %:



It is rather difficult to judge of the specific method used to obtain the commercial stilbene samples. Nevertheless, taking into account relatively low cost of the initial reagents (styrene, halobenzenes, halotoluenes), the cross-combination reactions cata-

X	Reagent/Catalyst	Stilbene yield, %	Ref.
Cl	CsOAc/PdCl[C <sub>6</sub> H <sub>3</sub> (OP(i-Pr) <sub>2</sub> ) <sub>2</sub> ]	99	19
	Bu <sub>4</sub> NBr/Bu <sub>3</sub> N/Pd[0]	98	20
	Bu <sub>4</sub> NBr/Ca(OH) <sub>2</sub> /Pd on NaY zeolite	90	21
	(PPh <sub>3</sub> ) <sub>2</sub> NiCl <sub>2</sub> , PPh <sub>3</sub> , zinc, pyridine	92	17

lyzed by transition metals (two latter reactions) might be supposed. In large-scale syntheses, the yields are usually somewhat lower than those described in literature, and polyarylsubstituted ethylenes, polycyclic aromatics, and the reduction products thereof could be expected as the impurities:



In this work, stilbene was obtained by benzalazine pyrolysis being carried out in a steel reactor of 1 L capacity with a screwed cap provided by two nipples for thermocouples and a glass tapping with air cooler for distillation of the released substances. The cooler was equipped with an electric heater to avoid the premature crystallization of stilbene being distilled off. The reactor was heated by an electrical bath, the heating temperature being controlled by the depth of the reactor immersion into the furnace. A typical benzalazine charge was 500 g. The system was sealed, the gas exit tube connected to the receiver was immersed into a flask with benzene. The decomposition rate was estimated using the release intensity of nitrogen bubbling through benzene. At the end of distillation, the furnace was switched out, the solidified distillate consisting of stilbene and benzonitrile was melted, placed into a mortar and ground. The mass was placed onto a filter, pressed thoroughly, washed with isopropanol (3×50 μL), pressed thoroughly again, and dried at 35–40°C. The stilbene yield was 100 g (23 %), m.p. 121–123°C. The oil separated from stilbene consisted mainly of benzonitrile.

For purification, the stilbene so obtained was recrystallized twice using dichloroethane (170 mL) with 10–15 g active carbon and washed on the filter with cold

Table 1. Summarized results of gas chromatographic analysis of stilbene samples \*)

Component	Stilbene from Merck				Stilbene from Fluka		Stilbene synthesized from benzalazine
	Initial	Recryst. From dichloroethane	Purified by direct. cryst.	Direct. cryst. + sublimation	Initial	Direct. cryst. + sublimation	
Benzonitrile	–	–	–	–	–	–	0.04
Biphenyl	0.04	0.02	<0.01	<0.01	0.03	<0.01	0.16
Dibenzyl	0.67	0.13	0.10	0.07	0.60	0.16	2.01
<i>cis</i> -Stilbene	<0.1	–	–	–	<0.1	–	Not found
<i>trans</i> -Stilbene	97.96	99.33	99.67	99.80	98.76	99.52	97.79
X-impurity	1.33	0.52	0.22	0.12	0.61	0.31	~(0.02–0.04)

\*) Values are presented in wt %. Relative error of the impurity mass fraction within the measured range (0.01 to 1.0 wt %) does not exceed 10 %.

dichloroethane. The product was dried at 35–40°C. The yield was 80 g (18.5 %), m.p. 123°C (reference value for *trans*-stilbene 124°C [1]). The product was further purified using zone melting or vertical directed crystallization. Using the final product, crystals were grown and the scintillation characteristics thereof were examined. To vary and extend the raw material sources for scintillation quality stilbene manufacturing, stilbene lots were purchased at Merck (Germany; synthetic grade) and at Fluka (Switzerland; scintillation grade). Those stilbene samples were purified additionally using the above techniques.

To monitor the purification process, gas chromatography (GC) method was used that was optimized for determination of most probable impurities in stilbene. Both the initial stilbene purified by various methods and stilbene single crystals were studied (a total of 25 samples). To identify the impurities, retention time values relative to *trans*-stilbene were determined for most typical impurities being formed at stilbene syntheses using various methods. When preparing the model mixture, sequential addition of individual compounds was used. The additives (benzonitrile, benzaldehyde, biphenyl, dibenzyl, acenaphthene, benzoic acid, tolan, anthracene, phenanthrene, fluorenone, benzoin) of at least analytical purity grade were used. Benzalazine and benzylidiphenyls were obtained in our laboratory and the individuality thereof was proved by GC and by comparison with known physicochemical constants. *Cis*-stilbene was prepared from *trans*-stilbene using UV irradiation of enriched isooctane solution. Ortho-, meta-, and para-terphenyl isomers that are not di-

rectly related to the stilbene synthesis products were of interest as reference substances in determination of gas chromatography retention characteristics under fixed experimental conditions. Those compounds were separated out of technical terphenyl using fractional crystallization.

The following measurement procedures were used:

*Procedure 1.* Gas chromatograph "Kris-tall 2000" controlled by IBM Pentium PC. Packed glass column 3 m×3 mm, Chromaton Super with 5 % FFAP (polyethyleneglycol 20000 reaction product with 2-nitroterephthalic acid); PID; carrier gas nitrogen, volume flow rate 25 cm<sup>3</sup>/min; column temp. 180 and 220°C, evaporator temp. 320°C, detector temp. 250°C. Sample volume 1–2 µL in warmed toluene solution.

*Procedure 2.* Gas chromatograph "Tswet 500" (model 530) connected to PC using a "Multispektr" interface. Packed glass column 2 m×3 mm, Chromaton Super with 5 % polydimethylsiloxane (OV-1); PID; carrier gas nitrogen, volume flow rate 20 cm<sup>3</sup>/min; column temp. 180°C, evaporator temp. 310°C, detector temp. 220°C. Sample volume 1–2 µL in warmed toluene solution.

*Procedure 3.* Gas chromatograph Varian CP-3800 with mass detector Varian 1200L. Quartz capillary column CP-Sil 5CB 50 m×0.25 mm; stationary phase polydimethylsiloxane. Evaporator temp. 300°C. Column temperature program: 70°C for 1 min, heating rate 20 deg/min up to 300°C, 300°C for 10 min. Detector ionizing chamber temp 250°C. Electron impact ionization, 70 eV.

Table 2. Gas-chromatographic retention characteristics <sup>\*)</sup> of compounds modeling the most probable impurities in *trans*-stilbene (Procedure 1, column temp. 220°C)

No.	Compound	Mol. mass	M.p., °C	$t'_R$ , min
1.	Benzonitrile	103.13	-13	0.90
2.	Benzaldehyde	106.13	-26	1.05
3.	Biphenyl	154.21	69	2.84
4.	Dibenzyl	182.27	52.5	3.65
5.	<i>cis</i> -Stilbene	180.25	~6	3.92
6.	Acenaphthene	154.21	95	4.05
7.	Benzoic acid	122.05	122	7.68
8.	Tolan	178.24	62.5	8.25
9.	<i>trans</i> -Stilbene	180.25	124	10.00
10.	Ortho-Terphenyl	230.31	56-59	14.56
11.	Anthracene	178.24	216	18.00
12.	Phenanthrene	178.24	101	18.00
13.	Fluorenone	180.20	84	19.20
14.	X-impurity	-	-	19.20
15.	2-Benzylbiphenyl	244.34	54	21.00
16.	Benzoin	212.25	133	22.20
17.	Benzalazine	208.26	93	30.50
18.	meta-Terphenyl	230.31	86-87	51.27
19.	4-Benzylidiphenyl	244.34	85	60.55
20.	para-Terphenyl	230.31	213	61.23

Absolute adjusted retention time calculated as  $t'_{Ri} = t_{Ri} - t_0$  where  $t_0$  is the retention time of non-sorbable compound (methane) that is 0.6 min. Relative retention time of a component  $t'_{Ri,rel} = (t_{Ri} - t_0) / (t_{Rstilbene} - t_0)$ .

In some stilbene samples, in particular, in those obtained from the Merck and Fluka initial materials, an impurity with retention time exceeding that of stilbene has been found besides of the usual biphenyl, dibenzyl, and *cis*-stilbene traces. In this work, that impurity has been referred to as X-impurity, see Table 1. The measured light yield values for the crystals grown from those stilbene samples amount 50 to 70 % of that for reference crystals (stilbene obtained from benzalazine). A complex combination of various purification techniques made it possible to reduce the X-impurity concentration down to 0.1-0.3 wt % and no further reduction of that characteristic was attained. It is to note that even after the X-impurity level was reduced down to the above minimum, the light yield of the grown crystals remained relatively low, while the dibenzyl impurity did not influence the light yield essentially even at its

Table 3. Gas-chromatographic retention characteristics of some studied compounds and X-impurity (improved measurements)

Compound	$t'_R$ , min at $t_0 = 0.63$ min	$t'_{R,rel}$
Biphenyl	5.97	0.20
Dibenzyl	8.40	0.29
<i>cis</i> -Stilbene	10.42	0.36
<i>trans</i> -Stilbene	28.95	1.00
Anthracene + phenanthrene	54.95	1.90
Fluorenone	58.50	2.02
X-impurity	61.45	2.12

Table 4. Retention characteristics of the model mixture components on a column with non-polar sorbent at 180°C

Compound	$t'_R$ , min at $t_0 = 0.55$ min	$t'_{R,rel}$
Dibenzyl	3.20	0.50
<i>cis</i> -Stilbene	4.00	0.62
<i>trans</i> -Stilbene	6.45	1.00
Fluorenone	7.45	1.16
X-impurity	11.20	1.74

level about 2 wt %. It was assumed that the X-impurity influences negatively the excitation energy transfer from the matrix to the emission centers in the crystal and enters easily the *trans*-stilbene crystal lattice. The latter is confirmed indirectly by difficulty of its removal using the crystallization purification methods.

To identify the unknown impurity, the retention characteristics of all the compounds used in the study were measured using Procedure 1 and compared with the similar value for the X-impurity, Table 2. The column temperature 220°C is the optimum for separation of the multicomponent model mixture. The preliminary conclusion from the Table 2 that the retention time is coincident for the X-impurity and fluorenone has been, however, not confirmed in the further improved experiment carried out using Procedure 1 but at column temp. 180°C (Table 3). The X-impurity and fluorenone have shown different retention values also when being chromatographed on a column with non-polar sorbent (Procedure 2; results see Table 4).

The X-impurity has not shown any significant shift in retention characteristics in relation to other mixture components when chromatographed using polar and non-polar stationary phases. Thus, that impurity was

assumed to belong also to polycyclic hydrocarbons differing from stilbene by one phenyl radical and most likely doing not contain any heteroatom. Our attempt to identify that impurity using IR spectroscopy and high resolution NMR (Varian Mercury VX-200 instrument) was unsuccessful. No differences were revealed between the crystal samples studied, most probably due to the impurity concentration too low for reliable detection.

That problem was solved using gas chromatography-mass-spectrometry (GC-MS, Procedure 3). The molecular mass of the impurity has been found to be 192. This result is consistent at the highest probability (86–88 %) with two possible compounds, 1-methylphenanthrene and 4-methylphenanthrene. More probable is just 1-methylphenanthrene that has the melting point (123°C) closest to that of *trans*-stilbene. It is logical to assume that 1-methylphenanthrene forms isomorphic crystals with *trans*-stilbene. This could explain, in particular, the found low efficiency of stilbene purification by zone melting. The definitive conclusion on the X-impurity nature and its influence on scintillation properties of stilbene could be drawn either using the preparative isolation of the impurity and its structure determination, or introducing purposefully methylphenanthrenes into certain pure scintillator samples.

Thus, combining chromatography and mass-spectrometry techniques, the 1-methylphenanthrene impurity has been identified in *trans*-stilbene samples and accurate values of absolute and relative retention time have been measured for probable accompanying components at fixed conditions of gas chromatographic analysis of raw stilbene. The results obtained make it possible to use in the production control of raw material and purified stilbene the relatively inexpensive and operative GC analysis using packed columns of traditional gas chromatographs and no make use of expensive methods (NMR, GC-MS) in routine work. The studies of scintillation *trans*-stilbene impurity composition make a base for more precise technical requirements and

specifications for raw stilbene aimed at optimization and efficiency improvement of the crystal growth technology.

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**Визначення складу побічних продуктів синтезу  
*транс*-стильбену методами газової хроматографії  
та хромато-мас-спектрометрії**

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За допомогою комбінації методів газової хроматографії та хромато-мас-спектрометрії досліджено домішковий склад *транс*-стильбену, одержаного синтетичним шляхом та очищеного різними способами. Одержані результати дозволили ідентифікувати лімітовані домішки та уточнити технологію одержання сцинтиляційного *транс*-стильбену.