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Chlorination of *trans*-1,2-Diarylethenes in Chloroform and Acetic Acid

V. N. Britsun, Yu. A. Serguchev, and N. I. Ganushchak

Institute of Organic Chemistry, Academy of Sciences of the Ukraine, Kiev, Ukraine
Franko Lviv National University, Lviv, Ukraine

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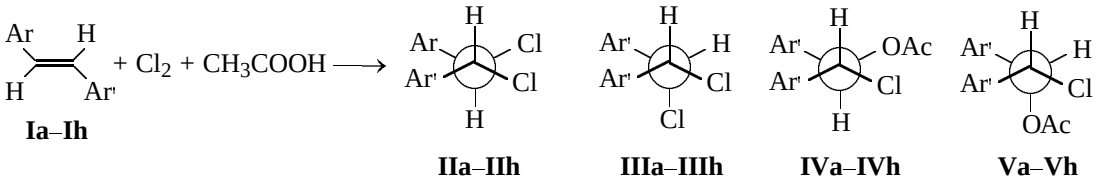
Abstract — When chlorinated in chloroform, (*E*)-stilbenes bearing electron-donor substituents in the *para* position of the benzene ring give *threo*-1,2-diaryl-1,2-dichloroethanes, while *meta*-substituted (*E*)-stilbenes, predominantly *erythro* isomers, irrespective of the nature of the substituent. The reactions in acetic acid result in preferential formation of *threo*-1,2-dichloro- and *threo*-1-acetoxy-1,2-diaryl-2-chloroethanes.

Earlier we showed that the chlorination of (*E*)-stilbene in the presence of pyridine *N*-oxide yields, along with chloroalkoxypyridinium chloride formed by conjugate addition, 1,2-diphenyl-1,2-dichloroethane [1, 2]. It was also found in that works that the chlorination products are mostly *threo* isomers, whereas the reactions of (*E*)-stilbene with benzeneselenenyl chloride [3] and sulfur dichloride [4] result in preferential formation of *erythro*-1,2-diphenyl-1,2-dichloroethane, while the reactions with phosphorus pentachloride [5] and dichloroiodobenzene [6] yield mixtures of the *erythro* and *threo* forms in a ratio depending on reaction conditions.

For detailed study of the products and stereochemistry of the reaction, we performed chlorination of stilbene, *p*-methoxystilbene, *p*-nitrostilbene, *p*-chlorostilbene, *m*-(trifluoromethyl)stilbene, *m*-methylstilbene, *p*,*p*'-dimethoxystilbene, and *p*,*p*'-dichlorostilbene in chloroform and acetic acid. It was found that the reactions in chloroform give 1,2-diaryl-1,2-dichloroethanes in the *threo* (**II**) and *erythro* (**III**) forms. The reactions in acetic acid afford, along with dichlorides **II** and **III**, 1-acetoxy-1,2-diaryl-2-chloroethanes in the *threo* (**IV**) and *erythro* (**V**) forms.



Ia–Ih **IIa–IIh** **IIIa–IIIh** **IVa–IVh** **Va–Vh**

Ar = Ar' = C_6H_5 (**a**); Ar = $C_6H_4OCH_3$-*p*, Ar' = C_6H_5 (**b**); Ar = $C_6H_4NO_2$-*p*, Ar' = C_6H_5 (**c**); Ar = C_6H_4Cl-*p*, Ar' = C_6H_5 (**d**); Ar = $C_6H_4CF_3$-*m*, Ar' = C_6H_5 (**e**); Ar = $C_6H_4CH_3$-*m*, Ar' = C_6H_5 (**f**); Ar = Ar' = $C_6H_4OCH_3$-*p* (**g**); Ar = Ar' = C_6H_4Cl-*p* (**h**).

The *threo*- and *erythro*-1,2-diaryl-1,2-dichloroethanes **II, III** and *threo*- and *erythro*-1-acetoxy-1,2-diaryl-2-chloroethanes **IV, V** were identified and the isomeric ratios were determined by ^{1}H NMR spectroscopy by the chemical shifts of the CHCl and C*H*·$OCOCH_3$ protons, which were earlier used for identification of chlorination products of stilbene and cynnamic esters [3, 7, 8]. The CHCl proton signals of 1,2-diaryl-1,2-dichloroethanes **II** and **III** are near 5.2 ppm, while the C*H*$OCOCH_3$ methine proton signals of 1-acetoxy-1,2-diaryl-2-chloroethanes **IV** and **V**, near 6.2 ppm. Therefore, *threo*- and *erythro*-1,2-dichlorides **II**, **III** and *threo*- and *erythro*-1-chloro-2-acetates **IV** and **V** were identified according to [3, 7, 8], taking into account that characteristic signals of the *threo* form are downfield from those of the *erythro* form [δ, ppm: CHCl: 5.14–5.34 (**II**) and 5.08–5.26 (**III**); C**H**$OCOCH_3$: 6.06–6.20 (**IV**) and 6.03–6.14 (**V**)]. The characteristic signals of the *threo* form have lower coupling constants compared with

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Table 1. Chlorination of *trans*-1,2-diarylethenes **Ia**–**Ih** in chloroform

trans-1,2-Diaryl-ethene	Chlorination products	**II** : **III** ratio	δ(C*H*Cl), ppm	
			II	**III**
Ia	**IIa, IIIa**	66:33	5.23	5.21
Ib	**IIb, IIIb**	60:40	5.20, 5.22	5.15, 5.19
Ic	**IIc, IIIc**	38:62	5.31, 5.34	5.22, 5.26
Id	**IId, IIId**	69:31	5.20, 5.22	5.16, 5.19
Ie	**IIe, IIIe**	32:68	5.26, 5.28	5.19, 5.23
If	**IIf, IIIf**	33:67	5.22, 5.24	5.17, 5.20
Ig	**IIg, IIIg**	50:50	5.14	5.08
Ih	**IIh, IIIh**	65:35	5.18	5.12

Table 2. Chlorination of *trans*-1,2-diarylethenes **Ia**–**Ih** in acetic acid

trans-1,2-Diaryl-ethene	Chlorination products	Ratio		
		II + **III** : **IV** + **V**	**II** : **III**	**IV** : **V**
Ia	**IIa, IIIa, IVa, Va**	75 : 25	78 : 22	60 : 40
Ib[a]	**IIb, IIIb, IVb, Vb**	–	59 : 41	–
Ic	**IIc, IIIc, IVc, Vc**	74 : 26	65 : 35	70 : 30
Id	**IId, IIId, IVd, Vd**	76 : 24	77 : 23	53 : 47
Ie	**IIe, IIIe, IVe, Ve**	65 : 35	47 : 53	71 : 29
If	**IIf, IIIf, IVf, Vf**	81 : 19	46 : 54	80 : 29
Ig[a]	**IIg, IIIg, IVg, Vg**	–	62 : 38	–
Ih	**IIh, IIIh, IVh, Vh**	77 : 23	80 : 20	55 : 45

[a] With *p*-methoxystilbene (**Ib**) and *p*,*p*'-dimethoxystilbene (**Ig**), no 1-acetoxy-2-chloro-1,2-diarylethanes are formed.

those of the *erythro* form both for 1,2-diaryl-1,2-dichloroethanes and for 1-acetoxy-1,2-diaryl-2-chloroethanes [*J*, Hz: 1,2-diaryl-1,2-dichloroethanes: 5.7–6.9 (**II**) and 9.2–12.3 (**III**); 1-acetoxy-1,2-diaryl-2-chloroethanes: 6.3–7.8 (**V**) and 7.4–9.8 (**V**)]. The results of the chlorination of 1,2-diarylethenes **I** in chloroform and the characteristic ^{1}H NMR signals of the chlrination products are listed in Table 1. As seen from Table 1, in chloroform, stilbene, *p*-methoxystilbene, *p*-chlorostilbene, and *p*,*p*'-dichlorostilbene yield more *threo*-1,2-diaryl-1,2-dichloroethanes **IIa, IIb, IId**, and **IIh** (60–69%) and less *erythro* isomers **IIIa, IIIb, IIId**, and **IIIh** (31–40%). *p*-Nitrostilbene and 1,2-diarylethenes with electron-donor and electron-acceptor substituents in the *meta* position [*m*-(trifluoromethyl)-stilbene and *m*-methylstilbene] give more *erythro* isomers **IIIc, IIIe, IIIf** (62–68%) and less *threo* isomers **IIc, IIe, IIf** (32–38%).

The chlorination of *p*,*p*'-dimethoxystilbene in chloroform gives a ~1 : 1 mixture of *threo* and *erythro* isomers **IIh** and **IIIh**.

Tables 2–4 list the results of the chlorination of substituted stilbenes **I** in acetic acid, as well as the characteristic ^{1}H NMR signals and coupling constants of chlorination products **IV** and **V**. As follows of the tabulated data, the major products of the chlorination of *trans*-1,2-diarylethenes in acetic acid are 1,2-diaryl-1,2-dichloroethanes **II** and **III** (65–81%), while the products of conjugate addition, 1-acetoxy-1,2-diaryl-2-chloroethanes **IV** and **V**, are formed in smaller amounts (19–35%). With *p*-methoxystilbene and *p*,*p*'-dimethoxystilbenes, no 1-acetoxy-1,2-diaryl-2-chloroethanes **IV** and **V** were found. It should be noted that the chlorination of methyl *p*-methoxycynnamate in acetic acid, too, involved no conjugate addition [8].

These results can be interpreted in terms of Shilov's trimolecular donor–acceptor principle (D → M → A principle) [9]. According to this principle, reaction of a donor (D), in our case acetate ion, with

Table 3. ^{1}H NMR spectra of 1-acetoxy-1,2-diaryl-2-chloroethanes **IV** and **V** in $CDCl_3$ (δ, ppm)

trans-1,2-Diaryl-ethene	**IV**			**V**		
	C*H*OCOCH$_3$	CHCl	OCOCH$_3$	C*H*OCOCH$_3$	CHCl	OCOCH$_3$
Ia	6.15, 6.17	5.11, 5.13	2.14	6.11, 6.14	5.09, 5.12	1.93
Ic	6.18, 6.20	5.19, 5.21	2.16	6.10, 6.14	5.14, 5.18	2.01
Id	6.12, 6.14	5.10, 5.12	2.14	6.05, 6.08	5.08, 5.11	1.96
Ie	6.14, 6.16	5.16, 5.18	2.15	6.08, 6.11	5.10, 5.13	1.97
If	6.12, 6.15	5.10, 5.13	2.13	6.08, 6.12	5.03, 5.07	2.05
Ih	6.08, 6.10	5.06, 5.08	2.15	6.03, 6.06	5.02, 5.05	1.99

a π complex (M → A), where M is stilbene and A is chlorine, should favor ionization of the π complex. Therewith, the stroger ionized the π complex, the less the nucleophilic species will affect the reaction energy and products. Apparently, in the chlorination of stilbenes with such strong electron-donor substituents as methoxy groups, the π complex transforms into a cationic intermediate the limiting reaction stage; this process does not involve acetate ions of the solvent, and the reaction product is formed via reaction of the carbenium ion with an internal chloride ion. By contrast, in the chlorination of less reactive stilbenes, ionization of the π complex in the limiting stage involves solvent molecules; as a result, according to the trimolecular mechanism, the products are 1-acetoxy-1,2-diaryl-2-chloroethanes.

1,2-Diaryl-1,2-dichloroethanes from *para*-substituted stilbenes are formed predominantly as *threo* isomers **IIb**–**IId, IIg, IIh** (59–80%), and from *meta*-substituted stilbenes give mixtures of *threo* (**IIe, IIf**) and *erythro* (**IIIe, IIIf**) isomers in roughly equal amounts. 1-Acetoxy-1,2-diaryl-2-chloroethanes in all cases are predominanly formed as *threo* isomers **IV** (53–80%).

It should be noted that the chlorination of unsymmetrical stilbenes in acetic acid can give rise to two regioisomers, 2-aryl-1-acetoxy-1-phenyl-2-chloroethanes **A** and 1-aryl-1-acetoxy-2-phenyl-2-chloroethanes **B**.

$ArCHClCH(OCOCH_3)C_6H_5$ $ArCH(OCOCH_3)CHClC_6H_5$
A **B**

However, as follows from the ^{1}H NMR spectra, the reaction occurs regioselectively and gives a single isomer. Regioisomeric assessment was performed on as example of conjugate chlorination of 1-phenyl-2-(*p*-chlorophenyl)ethene (**Id**), using the chemical shifts of the C*H*OCOCH$_3$ and CHCl groups of stilbenes **IVa** and **Va** and *p*,*p*'-dichlorostilbenes **IVh** and **Vh** (Table 3). We compared the chemical shifts of the C*H*OCOCH$_3$ and CHCl groups of the *threo* and *erythro* isomers of the regioisomer to be identified (**IVd**, **Vd**) with the corresponding chemical shifts of **IVa, IVh, Va** and **Vh**. The most close to each other proved to be the CHCl chemical shifts for *threo* form **IVd** (5.10, 5.12 ppm) and *threo* form **IVa** (5.11, 5.13 ppm) and respectively *erythro* form **Vd** (5.08, 5.11 ppm) and *erythro* form **Va** (5.09, 5.12 ppm), implying that compounds **IVd** and **Vd** have a C_6H_5CHCl fragment. A slightly worse correlation is between the C*H*OCOCH$_3$ chemical shifts of *threo* form **IVd** (6.12, 6.14 ppm) and *threo* form **IVh** (6.08, 6.10 ppm) and respectively *erythro* form **Vd** (6.05, 6.08 ppm) and *erythro* form **Vh** (6.03, 6.06 ppm), providing indirect evidence to show that **IVd** and **Vd** have a *p*-$ClC_6H_4CHOCOCH_3$ fragment. Thus, the ^{1}H NMR spectral evidence points to regioisomer **B**, *p*-$ClC_6H_4CH(OCOCH_3)CHClC_6H_5$ (a Markovnikov product). Therefore, there are strong grounds to beleive that unsymmetrical stilbenes are chlorinated by Markovnikov's rule. This proposal is confirmed by the results of the chlorination of cynnamoyl chloride and methyl cynnamate in the presence of pyridine *N*-oxide [2] and of the chlorination of substituted cynnamic esters in acetic acid [7, 8], where, too, a single Markovnikov isomer is formed.

Table 4. Spin–spin coupling constants (*J*, Hz) for characteristic proton signals of 1,2-diphenyl-1,2-dichloroethanes **II, III** and 1-acetoxy-1,2-diphenyl-2-chloroethanes (**IV, V**)

trans-1,2-Diarylethene	II	III	IV	V
Ia[a]	–	–	7.0	9.0
Ib[b]	6.3	12.3	–	–
Ic	6.9	11.7	6.3	7.4
Id	5.7	10.2	6.3	7.8
Ie	6.9	9.2	6.6	8.1
If	5.7	10.3	7.8	9.8
Ig[a,b]	–	–	–	–
Ih[a]	–	–	7.2	9.3

[a] The signal is not split. [b] 1-Acetoxy-1,2-diphenyl-2-chloroethanes are not formed.

Table 5. Melting points and elemental analyses of *erythro*-1,2-diaryl-1,2-dichloroethanes **IIIa**–**IIIh**

Comp. no.	mp, °C	Found Cl, %	Formula	Calculated Cl, %
IIIa	189	28.73	$C_{14}H_{12}Cl_2$	28.29
IIIb	190	25.11	$C_{15}H_{14}Cl_2O$	25.27
IIIc	208	24.15	$C_{14}H_{11}Cl_2NO_2$	23.99
IIId	178	37.81	$C_{14}H_{11}Cl_3$	37.43
IIIe	125	22.14	$C_{15}H_{11}Cl_2F_3$	22.26
IIIf	112	26.28	$C_{15}H_{14}Cl_2$	26.79
IIIg	190	22.41	$C_{16}H_{16}Cl_2O_2$	22.83
IIIh	193	44.62	$C_{14}H_{10}Cl_4$	44.38

EXPERIMENTAL

The ^{1}H NMR spectra in $CDCl_3$ were measured on a Varian VXR-300 spectrometer at 300 MHz, internal reference TMS.

trans-1,2-Diarylethenes were obtained by chlorination of arylethenes with aryldiazonium chlorides by the Meerwein reaction, followed by dehydrochlorination of 1,2-diaryl-1-chloroethanes [10].

1,2-Diaryl-1,2-dichloroethanes IIa–IIh and IIIa–IIIh. Chlorine, 2.5 mmol, was bubbled through a stirred solution of 2 mmol of *trans*-1,2-diarylethene in 10 ml of chloroform over the course of 15–20 min at 20–25°C. The mixture was stirred for 1 h, and the solvent was removed at room temperature. *erythro*-1,2-Diaryl-1,2-dichloroethanes were isolated by double recrystallization from ethanol. The melting points and elemental analyses of compounds **IIIa–IIIh** are listed in Table 5.

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