Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

Paolo Beltrame, Gabriele Cortili

Reactions of diaryl-halogeno-ethylenes with sodium ethoxide. - Part III. Cis- and trans-1-p-anisyl-1-phenyl-2-chloro-ethylenes. Reaction Products

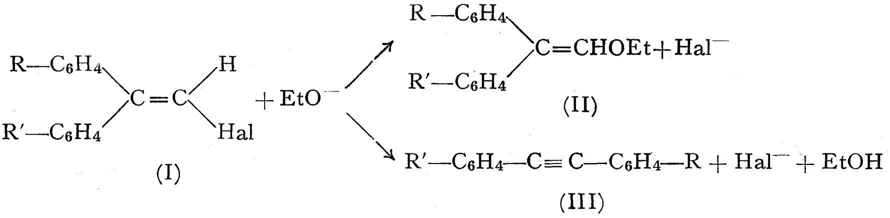
Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **39** (1965), n.5, p. 284–290.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1965_8_39_5_284_0>

Chimica fisica. — *Reactions of diaryl–halogeno–ethylenes with sodium ethoxide.* – Part III. Cis– *and* trans– *1–p–anisyl–1–phenyl–2–chloro–ethylenes. Reaction Products* (*). Nota di Paolo Beltrame e Gabriele Cortili, presentata (**) dal Corrisp. M. Simonetta.

The competitive α–elimination (F. B. W. rearrangement) [1] and nucleophilic substitution occurring in some 1,1–diaryl–2–halogeno–ethylenes (I) in the presence of ethoxide ion in ethanol were kinetically studied in a few cases [2] by varying R and R′ on one or both of the phenyl groups and varying the halogen.



The *cis*– and *trans*– 1–*p*–anisyl–1–phenyl–2–chloroethylenes (I ; Hal=Cl ; R = H , R′ = OMe and R = OMe , R′ = H respectively) were not so far examined. As it seemed worthwhile studying their behaviour, in order to compare them with the other compounds of the series, in particular with the corresponding bromo–ethylenes, both isomers of 1–*p*–anisyl–1–phenyl–2–chloroethylene have been prepared, identified as to their geometrical configuration and made to react with ethoxide ion.

EXPERIMENTAL.

Materials.—The solvent used for the U. V. measurements was methanol R. S. (C. Erba). Benzene of " cryoscopic " purity was employed for the determination of dipole moments.

Cis– *and* trans– *1–p–methoxyphenyl–1–phenyl–2–chloroethylene*: *p*–methoxy–acetophenone was prepared by standard methods [3] and subjected to Grignard reaction with phenyl magnesium bromide to give 1–*p*–methoxyphenyl–1–phenyl–ethylene [4]. The olefin (50 g) was dissolved in carbon tetrachloride (400 ml), and a solution of chlorine in the same solvent was

---

(*) Work done at the Istituto di Chimica fisica – Università di Milano.

(**) Nella seduta del 13 novembre 1965.

slowly added with stirring during 6 hr. at —30°. The reaction was followed by gas liquid chromatography (thermal conductivity detector; carrier gas hydrogen) on a 2–meter column of 10% Apiezon L grease on Celite at 230°. After the anisyl–phenyl–ethylene peak had just disappeared, and before an appreciable amount of higher chlorinated products could build up, the addition of chlorine was stopped; a 50% excess of pyridine (30 g) was added at —25°, the mixture left for 24 hr. at room temperature, the pyridine hydrochloride filtered off and the excess of base extracted with diluted hydrochloric acid. After evaporation of the carbon tetrachloride, a greenish oil (50 g) was obtained. The crude product was dissolved in ethanol (ca. 250 ml). A colorless solid crystallized at about —10° and was removed. On standing for several days, further crops could be isolated. After repeated recrystallization from ethanol, the solid had m.p. 58°. The primary ethanolic mother liquor was concentrated, cooled to ca. 0° and very slowly gave a colorless solid of different crystalline form; after recrystallization it had m.p. 53°. The mixed m.p. of the two solids was below room temperature. Analysis:

Calc. for $C_{15}H_{13}ClO$:	C 73.62 ;	H 5.36 ;	Cl 14.49%
Found for isomer m.p. 58° :	C 73.77 ;	H 5.49 ;	Cl 14.51
isomer m.p. 53° :	C 73.69 ;	H 5.27.	

p–methoxyphenyl–phenyl–acetylene was prepared from 1–*p*–anisyl–1–phenyl–2–chloroethylene (m.p. 58°) (1.64 g ; 6.7 mmoles) by reaction with potassium *t*–butoxide in *t*–butyl alcohol (0.78 g potassium in 50 ml of the alcohol) in a sealed tube at 120° for 7 days. The solution was acidified and extracted with ether, the ether layer dried and evaporated, yielding a slightly yellow product (1.2 g ; 5.8 mmoles; 86% yield). After crystallization from ethanol a colorless solid was obtained, m.p. 59°. Addition of bromine in $CHCl_3$ solution gave 4–methoxy–α, α′–dibromostilbene, m.p. 168°. The acetylenic product was identical with the one obtained from *cis*– and *trans*–1–*p*–anisyl–1–phenyl–2–bromoethylenes [2 *a*].

p–methoxyphenyl–phenyl–acetaldehyde was prepared according to A. Orechoff and M. Tiffenau [5] by reaction of 1–*p*–anisyl–1–phenyl–ethylene with yellow mercuric oxide and iodine, followed by prolonged contact with dry KOH. The mixture was extracted with ether, the ether layer treated with sodium bisulphite to give the addition compound of the aldehyde which crystallized within a few days. The crystals were washed and then the aldehyde was recovered as an oil by heating with aqueous sodium carbonate. Analysis:

Calc. for $C_{15}H_{14}O_2$:	C 79.62 ;	H 6.23%
Found:	C 79.31 ;	H 6.01.

Semicarbazone m.p. 127° (lit. 127–128°) [5].

Dipole moments.—Benzene solutions of the two isomers of *p*–anisyl–phenyl–chloroethylene were prepared in varying concentrations (weight fractions of solute w ranging from 0.005 to 0.03). The dielectric constants (e) were measured at 20° using a Dipolmeter DM 01 and refractive indexes at the same temperature (n) were determined with a Pulfrich refractometer. In each case several readings were taken on the Dipolmeter for the solution (N), the pure solvent (S) and the air (A) according to the sequence A–S–N–S–N–S–A–S–N–S–N–S–A, and average values were employed.

The orientation molar polarization P was obtained by the Guggenheim method [6], plotting e and n^2 versus w and evaluating the initial slopes of the graphs, α and ν, respectively. The points gave a reasonably straight line over the entire range of concentrations examined. Now

$$P = 3\frac{M}{d_1}\frac{\alpha - \nu}{(e_1 + 2)^2} \qquad (\text{cm}^3/\text{mole})$$

(M = molecular weight of the solute; d_1 = density and e_1 = dielectric constant of the pure solvent). The dipole moment μ was calculated by the equation:

$$\mu = 0.01282 \sqrt{PT} \ (\text{Debye})$$

Results:

	Isomer m.p. 58°	Isomer m.p. 53°
α	2.59	1.67
ν	0.33	0.25
P (cm³/mole)	103.2	64.8
μ (Debye)	2.23	1.76

($d_1 = 0.8794$; $e_1 = 2.2762$)

Applying a different treatment to the experimental data [7] a value of $\mu = 2.20$ D was obtained for the 58° isomer.

U. V. and I. R. spectra.—Ultraviolet spectra were measured on Beckmann DU and DK–2 spectrophotometers.

Trans–1–*p*–anisyl–1–phenyl–2–chloroethylene (m.p. 58°):

$$\lambda_{\max} = 266 \text{ m}\mu \ (\varepsilon = 17200) \ , \ 242 \text{ m}\mu \ (\varepsilon = 17900);$$

Cis isomer (m.p. 53°):

$$\lambda_{\max} = 260 \text{ m}\mu \ (\text{sh}) \ (\varepsilon = 12600) \ , \ 243 \text{ m}\mu \ (\varepsilon = 19100).$$

The formation of *p*-anisyl-phenyl-acetylene during the reactions was followed by measurements at 305 mμ, corresponding to the longest wavelength absorption maximum for that compound in methanol (ε = 25650) [2 *a*].

Infrared spectra were scanned on a Perkin-Elmer 21 apparatus with rock salt optics, using ca. 10% solutions in carbon disulphide (cf. fig. 1).

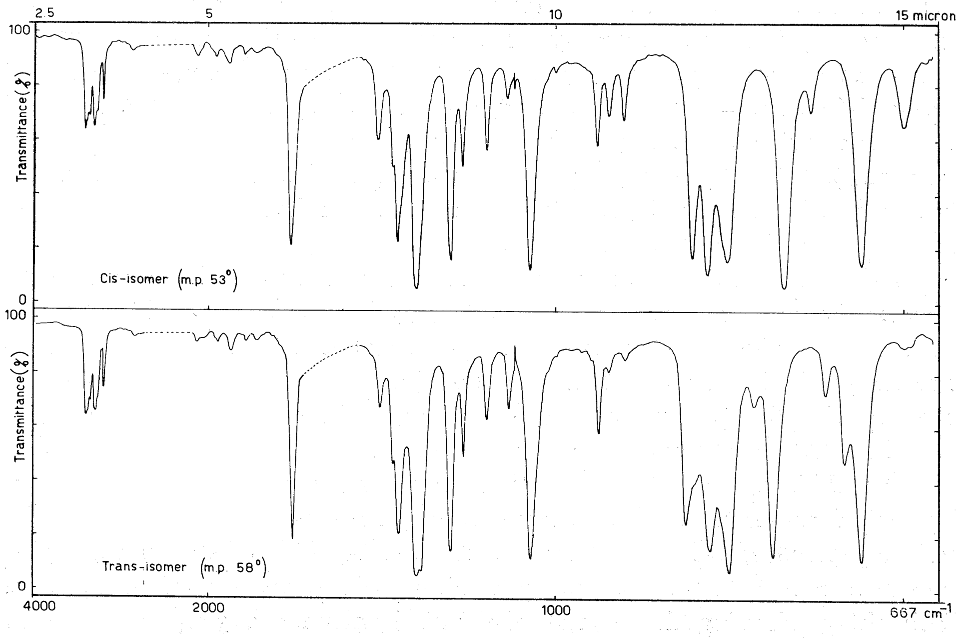


Fig. 1. - I.R. spectra of the isomers of 1-*p*-methoxyphenyl-1-phenyl-2-chloroethylene (ca. 10 % solution in carbon disulphide).

Products of reactions with ethoxide ion.—Reactions were carried in ethanolic solutions ca. 0.04 M in diaryl-chloroethylene and ca. 0.5 M in ethoxide ion. The overall reaction was followed by titration of chloride ion with silver nitrate. For the examination of products, the reaction solutions were concentrated *in vacuo*, mixed with water and extracted with ether; the ether layer was dried and the solvent removed. Since the oily product could not be purified by crystallization or column chromatography, physical methods were employed for the identification of products or their derivatives. Fractions of the samples, dissolved in methanol, were used to obtain U. V. spectra. Other fractions, dissolved in carbon disulphide, were examined by g.l.c. on a 2-meter column of 10% Carbowax 20M on Chromosorb W at 220° (flame ionization detector; carrier gas nitrogen).

Acid hydrolysis of the products was carried out by refluxing for 1.5 hr. with 20% hydrochloric acid. The hydrolysis products were then examined for *p*-anisyl-phenyl-acetaldehyde by g.l.c. After removing most of the aldehyde by prolonged treatment with a sodium bisulphite saturated solution, the residue was again injected into the gas–chromatograph. Pure *p*–anisyl–phenyl–acetylene was hydrolysed as a blank check.

Apart from minor bands due to impurities, the reaction product of the *trans*–isomer after 85% reaction, as determined by titration of chloride ion, gave three main peaks (relative retention times in brackets): unreacted starting material (1), acetylenic product (1.11) and " substitution product " (1.26). The oil examined weighed 3.0 g (starting from 4.89 g of organic chloride). After hydrolysis it was shown by g.l.c. that the " substitution product " had been almost completely removed and instead *p*–anisyl–phenyl–acetaldehyde appeared (rel. r.t. = 1.46). (The acetylene also disappeared and was replaced by a peak with rel. r.t. = 0.9; the same result was obtained for the control hydrolysis). G.L.C. of the hydrolysis product after bisulphite treatment showed very little aldehyde; *p*–anisyl–phenyl–acetaldehyde could be recovered from the addition compound.

A similar behaviour was shown by the product of the reaction of the *cis*–isomer: samples were taken at 17, 43, 62, 77 and 83% completion, and it was found consistently that the starting material disappeared, whilst a " substitution product » with the same retention time as the previous one appeared, together with the (less abundant) acetylenic product. Acid hydrolysis and bisulphite treatment gave the expected results.

The U.V. spectra of the reaction mixtures were obtained at different degrees of completion. The *trans*–isomer gave rise to products with the typical 305 mμ and 288 mμ bands of the *p*–anisyl–phenyl–acetylene, whilst the substrate band at 242 mμ and, to a minor extent, the one at 266 mμ were diminishing. During the reaction of the *cis*–isomer the 243 mμ band tended to disappear, and a new band at 268–270 mμ appeared with increasing intensity, as well as the absorption due to the acetylenic product.

RESULTS.

Geometrical isomers: The geometrical configurations of the isomers of 1–*p*–anisyl–1–phenyl–2–chloroethylene can be assigned on the basis of the dipole moments, as has been shown in the case of the corresponding bromo–ethylenes [2 *a*] [8]. For each *cis–trans* pair the higher dipole moment characterizes the *trans*–derivative (with *p*–anisyl *trans* to halogen).

The *trans* isomer of 1–*p*–anisyl–1–phenyl–2–bromoethylene had been found to have a moment 0.62 Debye higher than the corresponding *cis* derivative [2 *a*] (0.50 D according to other authors [8]). The present measurements for 1–*p*–anisyl–1–phenyl–2–chloroethylenes are 2.23 D for the higher melting isomer and 1.76 D for the lower melting isomer. The difference (0.47 D) is well above any experimental uncertainty, and it can be safely concluded that the 58° isomer has the *trans*, whilst the 53° isomer has the *cis* configuration.

The I. R. spectra of the isomers of 1–*p*–anisyl–1–phenyl–2–chloroethylene show many common features below 10 μ (see fig. 1). The bands at

1250 and 1037 cm^{-1}, and the one at 1340 cm^{-1} are assigned to the group = C—OCH$_3$; the C–H out of plane deformation bands in the region 11.5–14.5 μ, which are more sensitive to the geometry of the whole molecule, present the main differences, and show some analogies with the corresponding bromoethylenes, as can be seen from the data in Table I. The U.V. spectra show also interesting parallels (Table I).

TABLE I.

Parallels in I.R. and U.V. spectra of the cis–trans *pairs of 1–p–anisyl–1–phenyl–2–halogeno–ethylenes.*

Hal = Br [9]		Hal = Cl	
Cis (m.p. 61°)	*Trans* (m.p. 82°)	*Cis* (m.p. 53°)	*Trans* (m.p. 58°)
I.R. spectra (absorption maxima wavenumber).			
832 cm^{-1} (s)	835 cm^{-1} (s)	835 cm^{-1} (s)	842 cm^{-1} (s)
763 cm^{-1} (s)	770 cm^{-1} (s)	752 cm^{-1} (s)	761 cm^{-1} (s)
no band	709 cm^{-1} (w)	no band	706 cm^{-1} (w)
U.V. spectra (λ_{max}; ε values in parenthesis).			
262 mμ (sh) (13000)	270 mμ (19000)	260 mμ (sh) (12600)	266 mμ (17200)
246 mμ (17600)	246 mμ (14900)	243 mμ (19100)	242 mμ (17900)

Products identification: Although no separation of the products has been effected, physical and chemical data have been collected in order to prove that the main products of the reaction of both isomers with ethoxide ion in ethanol are 1–*p*–anisyl–1–phenyl–2–ethoxyethylenes (II; R = H , R′ = OMe) and *p*–anisyl–phenyl–acetylene (III; R = H , R′ = OMe). The acetylenic compound has been detected in both " *cis* " and " *trans* " reaction products by its U.V. absorption bands and by g.l.c., through comparison with a pure sample prepared under different conditions. Moreover the acetylenic product matched pure *p*–anisyl–phenyl–acetylene in its behaviour during the acid hydrolysis of the products, as followed by g.l.c. The *trans*–isomer gave a higher percentage of acetylenic product than the *cis*–isomer.

Of the gas chromatograms of the reaction mixtures, apart from the band of the starting compounds and neglecting small signals from impurities, only one other peak needed consideration; this was believed to arise from a substitution product, since on hydrolysis of the reaction mixture under acidic conditions the peak disappeared and a new one, having the same retention time as a pure sample of *p*–anisyl–phenyl–acetaldehyde, showed up. Furthermore, bisulphite solution removed most of the substance responsible for the new peak, and *p*–anisyl–phenyl–acetaldehyde could be recovered from the addition compound. The precursor of the aldehyde must then be unrearranged vinylic ether (cis and/or *trans* isomer, as in principle both isomers can be expected) (1).

The *cis* and the *trans* isomer could not be resolved by g.l.c., and no resolution was expected for the *cis* and *trans* ethers. The U.V. spectra of reaction mixtures from both *cis* and *trans* chloroethylenes showed that the ethers have a band around 268–270 mμ, *i.e.* in a region typical of a diphenyl–methylene group; however, it cannot be decided whether the ethers from *cis* or *trans* chloroethylenes have different or equal U.V. absorptions. Therefore, no conclusion can be drawn with respect to the stereospecificity of the substitution reaction.

Acknowledgement: We are indebted to the Italian C.N.R. for financial aid.

REFERENCES.

[1] P. FRITSCH, W. P. BUTTENBERG, H. WIECHELL, « Annalen », *279*, 319, 324, 337 (1894),
[2] (*a*) P. BELTRAME, S. CARRÀ, « Gazz. Chim. Ital. », *91*, 889 (1961); (*b*) P. BELTRAME. G. FAVINI, « Gazz. Chim. Ital. », *93*, 757 (1963).
[3] C. R. NOLLER, R. ADAMS, « J. Am. Chem. Soc. », *46*, 1889 (1924).
[4] C. D. HURD, C. N. WEBB, « J. Am. Chem. Soc. », *49*, 546 (1927).
[5] A. ORECHOFF, M. TIFFENAU, « Bull. Soc. Chim. » [4], *37*, 1417 (1925).
[6] J. W. SMITH, *Electric dipole moments*, Butterworth (London), 58 (1955).
[7] P. COHEN HENRIQUEZ, « Rec. Trav. Chim. », *3*, 327 (1935).
[8] W. M. JONES, R. DAMICO, « J. Am. Chem. Soc. », *85*, 2273 (1963).
[9] I. R. BELLOBONO, P. BELTRAME, unpublished results.

RIASSUNTO. — Gli isomeri *cis* e *trans* dell'1–fenil–1–*p*–metossifenil–2–cloroetilene sono stati preparati e separati, e la loro configurazione geometrica determinata in base ai momenti dipolari.

Tali composti reagiscono con ioni etilato dando in parte α–eliminazione e trasposizione a fenil–*p*–metossifenil–acetilene, in parte sostituzione nucleofila del cloro.

---

(1) The analysis reported above has also been applied to the products of the reaction between 1, 1–diphenyl–2–chloroethylene and ethoxide ion in ethanol, confirming the presence of the corresponding products (II) and (III) ($R = R' = H$) [1].