$$\begin{tikzcd} \begin{array}{c}\mathrm{SH_2}\\(1.26)\end{array} \arrow[r, "k^{ex}"] \arrow[d, "k_{OD}"] & \begin{array}{c}\mathrm{SHD}\\(1.53)\end{array} \arrow[r, "k^{ex}"] \arrow[d, "k_{OD}"] & \begin{array}{c}\mathrm{SD_2}\\(47.23)\end{array} \arrow[d, "k_{OD}"] \\ \begin{array}{c}\mathrm{PH_2}\\(1.44)\end{array} & \begin{array}{c}\mathrm{PHD}\\(2.82)\end{array} & \begin{array}{c}\mathrm{PD_2}\\(45.74)\end{array} \end{tikzcd} \quad (3)$$

We assume that the secondary isotope effects for hydrogen–deuterium exchange and hydrolysis can be neglected. With this assumption the rate constant ratio k_{ex}/k_{OD} can be calculated to be 34.[13] This value agrees well with the value of 27 which we obtained as described earlier in this article. With the assumption of the lack of a secondary isotope effect we can also calculate predicted percentages of PHD and PD_2 which should be obtained, knowing the ratio k_{ex}/k_{OD} and the percentages of SHD and SD_2 found. The values we calculate are 2.75% for PHD and 45.79% for PD_2. Considering our experimental error and the assumption involved in our calculation these values are in excellent agreement with the experimental data we have. Furthermore, according to the pathway assumed in eq 3 it would be expected that the percentage of PH_2 would exceed the percentage of SH_2 and the percentage of SD_2 should exceed that of PD_2. Even with a relatively small proportion of the hydrolysis reaction occurring by a carbanion mechanism such as that shown in eq 1 these relative percentages would be equal or reversed. The results, of course do show that $\% \ PH_2 > \% \ SH_2$ and that $\% \ SD_2 > \% \ PD_2$.

Finally, eq 2 can be ruled out as the mechanism of sultone solvolysis since the rate of deuterolysis of III containing deuterium atoms in the methylene group is somewhat faster under comparable conditions than the rate of hydrolysis of unlabeled III in unlabeled solvent. A substantial primary isotope effect would have been expected if eq 2 were correct with the deuterated compound reacting several times slower than the undeuterated one.[14]

From a variety of experimental approaches we conclude that mechanisms involving carbanion intermediates do not appear to be the predominant pathways by which five-membered cyclic sulfonates hydrolyze, as indicated earlier[6] by indirect evidence. The large rate enhancements we have observed for the hydrolyses of these compounds relative to their open-chain analogs must then reflect the differences in the rates of attack of hydroxide ion at the sulfur atoms in the cyclic and acyclic systems just as we have found for the corresponding sulfates. We have demonstrated thus that our methods provide reliable tools to determine whether or not carbanions lie along the reaction pathway in ester hydrolyses.

Acknowledgment. This investigation was supported in part by grants from the National Institutes of Health.

66.6% dioxane–deuterium oxide. In the presence of a large excess of deuterium oxide the deuterium exchange reactions can be treated as irreversible processes. The extent of deuterium incorporation in the hydrolysis products was determined after they were recyclized to the sultone.

[13] The formula used for the calculation is simply $k_{ex}/k_{OD} = [100 - \% PH_2 - \% SH_2]/2(\% PH_2)$: O. R. Zaborsky, Ph.D. Thesis, University of Chicago, 1968, p 136.

[14] From such measurements a k_{OH}/k_{OD} ratio of about 0.7 was obtained: K. Kudo, unpublished results confirmed by W. Berg.

Vinylic Cations from Solvolysis. II. The Stereochemistry of the SN1 Reaction of 1,2-Dianisyl-2-phenylvinyl Halides[1]

Zvi Rappoport and Yitzhak Apeloig

Contribution from the Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel. *Received May 23, 1969*

Abstract: *cis-* and *trans-*1,2-dianisyl-2-phenylvinyl bromide and chloride were prepared and their stereochemistry determined. Solvolysis in the presence of benzylthiolate and *p*-toluenethiolate ions in 80% ethanol, chloride ion in acetic acid and in dimethylformamide, and acetate ion in acetic acid gave *cis* and *trans* products derived from capture of the intermediate cation by the nucleophile, in 1:1 ratios. 1,2-Dianisyl-2-phenylethanone is formed on solvolysis in aqueous ethanol, formic acid, and dimethylformamide. Predictions regarding the stereochemistry of the SN1 vinylic substitution are discussed and it is concluded that the product-forming intermediate is a linear sp hybridized dissociated vinyl cation.

Although the interest in vinyl cations is increasing[2–5] many aspects of their chemistry are unknown. An important example is the structure of the cation formed during the solvolysis of vinyl halides or sulfonates.[5] The vinyl cation may be either linear, sp

---

[1] Part I. Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, 91, 5246 (1969).

[2] For leading references for formation of vinyl cations by electrophilic additions to acetylenes and allenes see ref 2 in ref 1.

[3] W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, 89, 1960 (1967).

[4] D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, 87, 863 (1965).

[5] (a) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 47, 194 (1964); (b) C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, 47, 1590 (1964); (c) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968); G. Modena, U. Tonellato, and F. Naso, *Chem. Commun.*, 1363 (1968); G. Modena and U. Tonellato, *ibid.*, 1676 (1968); (d) L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, 90, 7282 (1968); (e) S. A. Sherrod and R. G. Bergman, *ibid.*, 91, 2117 (1969); (f) M. Hanack and T. Bässler, *ibid.*, 91, 2117 (1969); (g) C. A. Grob and R. Spaar, *Tetrahedron Lett.*, 1439 (1969).

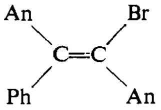
hybridized at the cationic center, or "bent," sp^2 hybridized with the empty orbital in the direction of the original location of the leaving group. Electronic and steric effects favor a linear geometry, but "bent" structures were also suggested[6] and cannot be discarded. Neighboring group participation, giving a bridged ion may be also important, although not observed yet in vinylic systems. Information regarding the structure of the product-forming intermediate and involvement of ion pairs can be obtained by studying the stereochemistry of the vinylic solvolysis reaction. Although this stereochemistry is virtually unknown, there is evidence that vinyl cations formed by addition of protons to triple bonds do not give equal amounts of *cis* and *trans* nucleophile-captured products even if they are stabilized by an α-aryl group.[7a,8]

Activated compounds for S$_N$1 solvolysis where competing reactions are minimized are α-anisyl-β,β-diarylvinyl halides. In continuation of our previous work[1] the stereochemistry of the reaction of *cis*- and *trans*-1,2-dianisyl-2-phenylvinyl halides with several nucleophiles was investigated. Kinetic evidence that carbonium ions are intermediates in these reactions will be presented in a forthcoming publication.[9]

Results

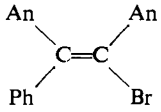
Structure Determination. *cis*- and *trans*-1,2-dianisyl-2-phenylethylenes, vinyl bromides and chlorides were prepared and separated. The geometrical relationship will be discussed in relation to the bromides which were mainly investigated, and briefly also for the chlorides and the ethylenes.

An old criterion to differentiate between geometrical isomers is based on the assumption of a higher melting point for the more symmetrical isomer.[10] If this is applicable to tetrasubstituted ethylenes, the isomer **1** with the two *trans* anisyl groups is more symmetrical, and the lower melting isomer **2** has the *cis* configuration.



1

trans, mp 135°



2

cis, mp 118°

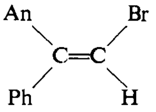
An = anisyl

Table I. Ultraviolet Spectra of Triarylvinyl Bromides in Cyclohexane

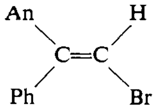
Compound	λ_{max}, mμ	ϵ	λ_{max}, mμ	ϵ
Ph An >C=C< Ph Br	239.5	22,000	302	11,600
An Ph >C=C< An Br	241.5	23,700	310	11,000
An Ph >C=C< Ph Br	239	20,000	303.5	10,700
An An >C=C< An Br	249	27,500	310.5	13,000
Ph An >C=C< An Br[a]	241	25,300	308	12,900
An An[b] >C=C< Ph Br	247.5	26,300	308	13,400

[a] High melting point. [b] Low melting point.

The dipole moments in benzene are 2.86 D for the low melting and 2.37 D for the high melting isomer. The anisyl group is electron donating as suggested for *p*-methoxystilbene[11] or from comparing moments of *p*-bromoanisole, anisole, and bromobenzene.[12] Calculation without a detailed knowledge of the conformation of the methoxy group may be misleading,[13] but the *trans* isomer will be the one with the lower dipole moment. The C–Br dipole is the main component of the moment as shown by the similar values for *cis*- and *trans*-α-bromostilbene[14] and bromobenzene. The dipole moments of *cis*- and *trans*-1-anisyl-1-phenyl-2-bromoethylenes **3** and **4** are, respectively, 1.68 and 2.30 D according to one source,[15] and 2.15 and 2.65 D according to another.[16] The calculated values are lower than the observed ones but the difference between them is similar.[16] From the latest values for **3** and **4**[15] and anisole, calculation (neglecting rotation of the methoxy group and assuming normal angles) gives 2.55 and 3.12 D for **1** and **2**, respectively. The values and the differences are close to the observed ones and support the assignments for **1** and **2**.



3



4

The uv spectra of triarylvinyl bromides containing phenyl and anisyl groups (Table I) show maxima at 302–310.5 mμ and about twice as intense maxima at 239–249 mμ. Suzuki[17] had treated the higher band of the similar spectra of triarylethylenes as due to the *trans*-

---

[6] P. E. Peterson and R. J. Kamat, *J. Amer. Chem. Soc.*, 88, 3152 (1966).

[7] (a) R. C. Fahey and D. J. Lee, *ibid.*, **88**, 5555 (1966); (b) P. E. Peterson and J. E. Duddey, *ibid.*, 88, 4990 (1966).

[8] A referee had commented that the presence of an α-aryl substituent in our system dictates a linear geometry for the vinyl cation, while this may not be the geometry of other vinyl cations. While we agree that the main factor stabilizing our ion is conjugation with the α-aryl group, and that the ion is probably linear, the stereochemistry of the substitution cannot be predicted *a priori*. Indeed, an aliphatic vinyl cation formed by addition of proton to the triple bond gave equal amounts of *cis* and *trans* products,[7b] while the ion derived from α-phenylpropyne gave different amounts.[7a] There is also some evidence that in our system the initially formed ion pairs partially retain their configuration.[9] Moreover, secondary α-aryl substituted saturated ions, *e.g.*, α-phenylethyl ions, which are at least as stable as our ions, give preference for inverted products on solvolysis. Finally, it is not at all clear if an ion derived from α-halostyrene substituted by β-acetate or β-*p*-dimethylaminophenyl groups which are favored in participation would not have a geometry dictated by participation, which would control the stereochemistry of the solvolysis. Such systems are now under investigation.

[9] Z. Rappoport and Y. Apeloig, paper submitted for publication in *J. Amer. Chem. Soc.*

[10] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 326–327.

[11] A. J. Boulton, G. M. Glover, M. H. Hutchinson, A. R. Katritzky, D. J. Short, and L. E. Sutton, *J. Chem. Soc.*, *B*, 822 (1966).

[12] A. L. McLellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

[13] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, pp 238–243.

[14] E. Bergmann, *J. Chem. Soc.*, 987 (1935).

[15] (a) P. Beltrame and S. Carrà, *Gazz. Chim. Ital.*, **91**, 889 (1961); (b) P. Beltrame, I. R. Bellobono, and A. Ferè, *J. Chem. Soc.*, *B*, 1165 (1966).

[16] W. M. Jones and R. Damico, *J. Amer. Chem. Soc.*, **85**, 2273 (1963).

[17] H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 389 (1960).

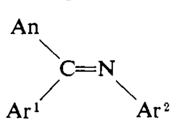
Table II. Nmr Spectra of Triarylethylenes and Triarylvinyl Bromides in Deuteriochloroform[a]

	X = H					X = Br			
Compound	MeO	*cis*-β-Ar	*trans*-β-Ar	α-Ar	H	MeO	*cis*-β-Ar	*trans*-β-Ar	α-Br
Ph An >C=C< Ph X	217.5	436	436	399	414	220	421	440	400.5
				424					435.5
An Ph >C=C< An X	226	410	410			219	421	402	
	227	436	436	425	410	228	428.5	447	*ca.* 444[b]
An An >C=C< An X	226		412	405		220	421	409	403.5
	229	420	432	438	420[c]	223	421.5	446	445
	231					228			
						195.5[d]	401[d]	404[d]	421[d]
						197			
							454	457	424
An Ph >C=C< Ph X						206.5			424
						232.5	431[b]	445[b]	448
An An >C=C< Ph X	221.5	410.5		399.5		218	393.5		400
			436.5		410			438.5	
	227	418.5		427.5		222	410.5		434
Ph An >C=C< An X	219		398.5	391.5		224		410	398.5
		428.5			398		419.5–421		
	224.5		420.5	412.5		228		431	435

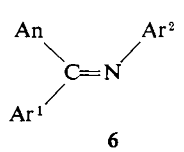
[a] *cis* and *trans* refer to the α-aryl group. When only one number is given the signal is a singlet; when two are given they refer to the anisyl protons. The one at the higher field is *ortho* to the methoxy group. [b] Split and centered at this position. [c] Uncertain assignment. [d] In hexadeuteriobenzene.

stilbene chromophore, concluding that all the aryl groups are twisted from the double bond plane. The longer wavelength maxima of **1** and **2** are at the same position, but the lower maxima, the nature of which is not completely understood,[18] do not coincide. However, the first three compounds (λ_{max} 240 ± 1.5 mμ) have *cis* anisyl and phenyl groups while the fourth one (λ_{max} 249 mμ) has two *cis* anisyl groups. Since λ_{max} = 241 mμ for the high melting and 247.5 mμ for the low melting isomer, this suggests for them structures in line with the dipole moments.

Nmr spectra are valuable in the structure determination. The aromatic protons of *trans*-stilbene,[19] *p*-methoxy and other stilbenes,[20] and α-methyl-α-bromostyrene[21] are multiplets at a lower field than the aromatic singlet or narrower multiplet of the *cis* isomers.[19-21] In the N-arylbenzophenone imines **5** and **6**[22] when Ar^1 = An, electron-donating substituents in Ar^2 cause a higher difference between the *ortho* and the *meta* protons (δ_{o-m}) of the *trans*-An than in the *cis* ring, the *trans* ring protons being always at lower field. When Ar^1 = Ph and Ar^2 = An the methoxyl of Ar^2 in **5** is at lower field than that in **6**.



5



6

The data fit the assumptions that in these compounds the *trans* system is more planar than the *cis* one and that the ring hydrogens are deshielded due to the ring current of the *trans* ring. From models of triarylethylenes the aryl *cis* to the hydrogen is almost coplanar with the double bond, while due to steric interference the two other rings cannot be simultaneously in the plane. The electronic factor favoring the conjugated *trans* stilbene unit probably has a buttressing effect forcing the β-aryl group to a perpendicular position while the α group is nearly in the plane, although the exact conformation of polyarylethylenes is controversial.[17,23] With the *trans* aryl groups more in the plane, the *cis* ring protons will be above the plane, shielded, and at a higher field than the *trans* ring protons.

While, from models, the favored conformations of **1** and **2** have three aryl groups perpendicular to the C=C plane, the uv data point to an appreciable conjugation. The steric hindrance is reduced in the conformation in which the two *trans* rings are twisted to about the same degree.[24] The remaining *cis* group is forced to a perpendicular position and its protons are again at higher field.

The predictions are borne out by the nmr data of Table II as shown by the assignments for 1-anisyl-2,2-diphenyl- and for trianisylvinyl bromides. The α-anisyl of **1** and **2** is at the same δ with the same δ_{o-m}. However, the phenyl group of the *cis* isomer is at the lowest field and the *cis*-anisyl group is at the highest with a lower δ_{o-m} value, compared to the *trans* isomer where the phenyl is at a higher field and the *trans* anisyl is at a lower field with a higher δ_{o-m} value. The positions of the methoxy signals are in line with those

---

(18) An explanation may follow the suggestion that the low wavelength maxima in stilbenes are due to the excited state in which one of the aryl groups is nearly coplanar with the double bond and the other one is at a right angle, not contributing to the resonance (ref 10, p 330). If the anisyl group is the one which is preferably coplanar owing to higher conjugation, and if the group *trans* to it is the perpendicular one, the absorption of our compounds would mainly involve interaction between *cis* groups and would give the higher wavelength in this region for the compounds with *cis* anisyl groups, as found.

(19) "Nmr Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, spectra 305, 306.

(20) H. Güsten and M. Salzwedel, *Tetrahedron*, **23**, 173, 187 (1967).

(21) D. R. Davis and J. D. Roberts, *J. Amer. Chem. Soc.*, 84, 2252 (1962).

(22) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, 88, 2775 (1966).

(23) R. N. Jones, *ibid.*, **65**, 1818 (1943).

(24) Both rings can be rotated in the same direction from the planar arrangement, and then the mutual deshielding is at maximum. On rotating in opposite directions but with the same angle, the deshielding is still larger than for the third aryl group.

of **5** and **6**.[22] That of the α-anisyl is at the highest field, followed by that of the *cis*-anisyl. The lowest signal is for an anisyl ring *trans* to a phenyl or preferably to an anisyl group.

Since the nmr assignments are in line with the other methods, nmr was used for assignments of other pairs. For example, from the similarity of the nmr of the chlorides and the bromides, the low and the high melting chloride are *cis* and *trans*, respectively. The structural assignments of the ethylenes and the vinyl acetates are based on similar data and agree with those based on melting points.

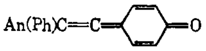
Mass Spectra. The mass spectra of **1** and **2** (Table III) are very similar. The base peak (*m/e* 315) corresponds to the vinyl cation **7** formed by the loss of

$$\mathrm{An(Ph)C{=}\overset{+}{C}An}$$

7

bromine from the molecular peak which is the second most intense one (85–90%). This fragmentation is similar to that of 1-bromo-2-(4-morpholino)-1,2-diphenylethylene,[25] where further fragmentations were more pronounced. All the other peaks (including those for Ar^+) are small, contain no bromine, and are probably derived from **7**. Small differences in their intensity may result from different geometries and energies of **7** derived from the two precursors.

Table III. Mass Spectra of 1,2-Dianisyl-2-phenylvinyl Halides[a]

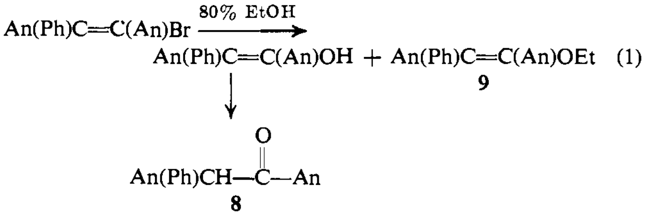
m/e	*cis*-Cl[b]	*trans*-Cl[b]	*cis*-Br[c]	*trans*-Br[c]	Assigned for ion
396			43	4.55	M (Br^{81})
394			42	44.5	M (Br^{79})
381, 379			0.2	0.2	M − Me
352	35	35			M (Cl^{37})
350	100	100			M (Cl^{35})
335	1.2	1.2			M − Me
315	30.5	29.5	100	100	**7**
300	4.3	4.3	2.3	3.3	
270	1.8	2.4	3.7	2.3	
257	1.5	1.5	3.8	2.0	
239	5.0	5.0	9.0	4.0	$AnC^+{=}CHAn$
229	3.0	3.0	5.0	2.4	
165	6.0	8.5	7.5	2.0	9-Fluorenyl$^+$
107	41	41	0.15	2.2	An^+
106	39	39	0.3	0.6	$(An–H)^+$
77	10.5	13.5	1.3	0.7	Ph^+

[a] The numbers refer to relative abundance. Most of the peaks with less than 5% were omitted. [b] Metastable peaks appear at *ca.* 283 corresponding to 350, 352 → 315 and to 315 → 300. [c] Metastable peaks appear at 251.5 and 283, corresponding to 394, 396 → 315 and to 300 → 315.

The mass spectra of the two chlorides are similar, but differ from that of **1** and **2**. The base peak is the molecular peak (*m/e* 350, 352) followed by intense An^+ and $(An–H)^+$ fragments. The peak for **7** is appreciable and fragments derived from it are small, but a chlorine-containing fragment is formed at M − 15 by the loss of a methyl group. The intensity ratio of the molecular peak to **7** for the bromides and the chlorides is similar to that of the haloenamines mentioned above.[25]

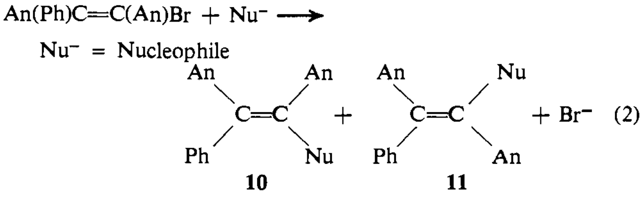
Fragments corresponding to the loss of CH_2Hal analogous to the M − 15 peaks in the spectra of stilbenes,[26] diphenylmethane,[27] 1,1-diphenylethylene,[28] and triarylethylenes[29] were not formed. A possible explanation is that **7** is stable, and the driving force for elimination with rearrangement to the 9-arylfluorenyl ion is low.[29] The high amount of the parent peak makes it also possible that sufficient energy for the process is not available.

Stereochemistry of the Solvolysis. Reactions in 80% Ethanol. The main solvolysis product (75–80%) of **1**, **2**, and the *cis*-chloride in basic 80% ethanol at 130–140° is 1,2-dianisyl-2-phenylethanone (**8**) formed *via* the corresponding enol (eq 1). Nmr of the crude reaction mixtures at the end of the reaction showed the presence of the ethyl ether (or ethers) **9** (25% from **1** and **2** and 20% from the chloride), and a solid with an ir consistent with **9** was obtained. Further attempts to separate the isomeric ethers were abandoned since the ethoxy signals are at the same δ in solvolysis mixtures from both isomers. However, because of this and since the isolated material from **1** and **2** have similar ir spectra, it is reasonable that the composition of **9** from solvolysis of **1** and **2** is similar.



$$\mathrm{An(Ph)C{=}C(An)Br \xrightarrow{80\%\ EtOH} An(Ph)C{=}C(An)OH + \underset{\mathbf{9}}{An(Ph)C{=}C(An)OEt}} \quad (1)$$
$$\downarrow$$
$$\mathrm{\underset{\mathbf{8}}{An(Ph)CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}An}}$$

p-Toluenethiolate ion captures effectively the trianisylvinyl cation in 80% ethanol,[1] and we hoped that the methyl signal would serve as a stereochemical marker. Reactions of either **1** or **2** with this nucleophile were complete after 5 hr at 120° (eq 2) and both gave products with identical ir spectra. The nmr (CCl_4) for reactions of both isomers was similar and integration of the aromatic, methoxyl and methyl protons corresponded to the vinyl *p*-toluenethiolate. Judged by the methyl triplet, **9** was present in less than 10%. Only one methyl singlet was observed at 123.5 cps, the same position as in trianisylvinyl- and 1-anisyl-2,2-diphenylvinyl *p*-toluenethiolate.[1]



$\mathrm{An(Ph)C{=}C(An)Br + Nu^- \longrightarrow}$ **10** + **11** $+ Br^-$ (2)

Nu^- = Nucleophile

a, Nu = SC_6H_4Me-*p*
b, Nu = $SCH_2C_6H_5$
c, Nu = AcO
d, Nu = Cl

The aromatic multiplet at 376–438 cps was complex. The methoxy region consists of four singlets at 207.5,

---

[25] S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, **90**, 2432 (1968).

[26] R. A. W. Johnstone and B. J. Z. Millard, *Naturforsch.*, **21a**, 604 (1966).

[27] S. Meyerson, H. Drews, and E. K. Fields, *J. Amer. Chem. Soc.*, **86**, 4964 (1964); J. H. D. Eland and C. J. Danby, *J. Chem. Soc.*, 5935 (1965).

[28] "Catalog of Mass Spectral Data," American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., spectrum No. 957.

[29] C. T. Pedersen, *Acta Chem. Scand.*, **22**, 706 (1968).

208.3, 210.3, and 214.5 cps (with a small shoulder) with relative ratios of 1:1:0.9:1.18. The last value is 1 if the shoulder is assumed to be due to the SH of unreacted *p*-toluenethiol (recognized by its 130.5 cps methyl). The four equal OMe signals require that **10a** and **11a** are formed in equal amounts.

Reaction in the presence of *benzylthiolate ion* was complete after 4.5 hr at 120° and crude reaction mixtures from **1** and **2** showed the same ir and nmr, corresponding to 80% triarylvinyl benzylthiolate and to 20% of the ether **9**. The methylene signals of **9**, **10b**, **11b**, and unreacted benzyl mercaptan and the methoxy signals appear in a narrow region. The signals from the *trans* bromide reaction and their relative ratios were 205 (0.5), 209 (1), 213 (1), 217 and 217.7 (together 2.75), 220 and 221 (together 2.9), and 223 cps (1.1). The corresponding ratios from the *cis* bromide were 0.4:1.1:0.65:2.4:2.5:1. In both, the methyl triplet was at 90 cps, a broad singlet of half of the aromatic protons at 433 and the other half as a multiplet at 390–430 cps.

Four equal methoxyl and two equal methylene signals in a ratio of 3:1 are predicted for a 1:1 ratio of **10b** to **11b**. In the spectra of the product from the *trans* bromide the 217, 217.7, 220, and 221 cps signals were similar in height and from integration these are the methoxy signals which are present in equal amounts. The broad 205 cps signal is probably due to the SH of unreacted benzyl mercaptan, and each of the other three singlets integrates as one proton. Even without knowledge of which of these belong to the methylenes of **10b** and **11b** they correspond to a 1:1 *cis* to *trans* ratio.

In the product from the *cis* bromide the methoxy signals are equal and those at 209.5 and 223 cps have a similar intensity, which is 0.4 of that of the methoxy signals. The error in the integration is relatively large. The 213.5 signal is too small to belong to the CH_2S of **10b** or **11b** and may be due to traces of benzyl mercaptan or to a side product. A 1:1 ratio of **10b** to **11b** is again obtained.

1-Anisyl-2,2-diphenylvinyl bromide was solvolyzed in the presence of benzylthiolate ion for 7 hr. The occurrence of two signals at 210 and 217 cps in a ratio of *ca.* 2:3 substantiates the assignment of the 210 cps signal to that of **10b** or **11b**.

Reactions in Acetic Acid. From mixtures of either **1** or **2** and *silver acetate* in acetic acid nearly quantitative yields of a mixture of the two vinyl acetates were obtained and separated. The high melting isomer showed a phenyl singlet at a higher field and methoxyl singlets at a lower field than the lower melting one. By arguments similar to those discussed for the bromides they were identified as the *cis* **10c** (Me at 111 cps) and the *trans* **11c** (Me at 114 cps) acetate, respectively.

Solvolysis of **1**, **2**, or **10d** in acetic acid containing 2 molar equiv of *sodium acetate* gave a mixture with signals at 111 and 114 cps in a 1:1 ratio. The 1:1 distribution was observed in kinetic experiments at 120° and 140° as early as after 10% solvolysis, and remained the same along the runs. The much faster silver acetate-catalyzed solvolysis gave after 1 hr at reflux or after 0.5 hr at 80°, with or without tenfold molar excess of sodium acetate, the same 1:1 ratio.

The acetolysis is accompanied by extensive ion pair and external return which causes $\mathbf{1} \rightleftharpoons \mathbf{2}$ isomerization.[9] While this is faster than solvolysis, the ratios of **1** to **2** at earlier reaction percentages beginning from either **1** or **2** differ sufficiently from one kinetic point to another and isomerization cannot be responsible for the observed stereochemistry. Moreover, the ratio of the bromides at equilibria is 37:63 and cannot lead to 1:1 acetate ratio.

Isomerization of the acetates in acetic acid containing sodium acetate is negligible under the reaction conditions. Less than 5% of **11c** is formed from **10c** after 46 hr, while the product distribution is 1:1 after less than 1 hr. Very little isomerization of **10c** was observed with excess added bromide ion after 150 hr. The equal *cis* to *trans* product distribution is therefore kinetically controlled.

Reaction of 0.04 *M* **1** in acetic acid containing 0.076 *M lithium chloride* for 280 min at 120° gave back 50% bromides in a 4:6 ratio of **1** to **2** and 50% of the chlorides in a 1:1 ratio of **10d** to **11d**. Under the same conditions the chloride isomerization is negligible and the corresponding ethylenes are only 12% isomerized. The ratio is again kinetically controlled.

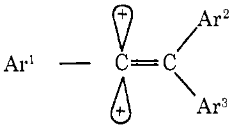
Reactions in Formic Acid. Solvolysis of 0.02 *M* of either **1** or **2** in dry formic acid (0.03 *M*) in sodium formate, or in formic acid containing 2% acetic anhydride was complete after 4 hr at reflux temperature and gave only the ketone **8**. The work-up included bicarbonate washing, which may hydrolyze the vinylic formate, and direct crystallization following the evaporation of the solvent was attempted, but **8** was again formed. Ir spectra of the reaction mixtures after evaporation of the solvent and without further treatment corresponded to that of **8**. Reflux of the *trans* ethylene for 48 hr in formic acid resulted in the formation of a 1:1 ratio of the *cis* to *trans* ethylenes.

Reactions in Dimethylformamide. Reaction of **1** and **2** in dry dimethylformamide gave only the ketone **8**. After 80 hr of reflux *ca.* 10% bromide still remained and **8** was isolated and identified. If 3% water is added to the solvent the reaction is complete after 40 hr. Reaction for 6 hr with an equimolar amount of silver fluoride gives over 70% of **8**. The recovered bromide is always partially isomerized.

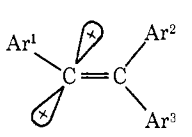
In reactions of a 2:1 ratio of *lithium chloride* to either **1** or **2** the formation of **8** complicates the stereochemical determination, but only traces of **8** are formed using a 40:1 ratio. After 5 hr at 120°, 25% chlorides were formed from **2**, but their ratio could not be determined, while the recovered bromides were in a ratio of 3:1 of *cis* to *trans*. After 80 hr, 80% of a 1:1 ratio of **10d** to **11d** was formed and after 136 hr the reaction was complete. Pure *trans* bromide was isolated from reaction mixtures of either **1** or **2** in yields of 14–20% and solid fractions rich in the *cis* isomer were also obtained. The isolated yield of the *trans* chloride is higher than its ratio in the chlorination mixture of the ethylenes (9:1, *cis* to *trans*). The chlorides isomerize at least ten times slower than the bromides solvolyze, and the 1:1 ratio must be kinetically controlled.

Discussion

Stereochemical Predictions for Vinylic SN1 Reactions. The stereochemistry of the vinylic SN1 substitution is dependent on the structure and the lifetime of the product-forming intermediate. The vinylic cation may have the linear sp hybridized structure **12** or the "bent" sp^2 hybridized one (**13**). Fahey[7] had noted that the most important energetic factor favoring the linear ion is "the promotion energy associated with the difference in a vacant sp^2 orbital and a vacant p orbital" which he



12



13

estimated to be roughly 75 kcal/mol. Other factors are enhanced stabilization due to shorter bonds with higher bond energies and the overlap between the vacant p and aromatic π orbitals.[7a] In our system such overlap is the main factor responsible for obtaining measurable rates as judged by the high response to substituent change[5a,d] and **12** is a likely possibility. Steric preference for **12** results from the absence of *cis* steric interactions which prevail in **13**.

If products are formed from **12**, which is free from the leaving group, attacks at both lobes of the empty p orbital have equal probability. The kinetically controlled products will be *cis* and *trans* isomers in a 1:1 ratio. We will call this process "racemization" in analogy to the racemization in saturated systems. While in compounds with one asymmetric center the 1:1 *d,l* ratio is thermodynamically favored, a 1:1 *cis* to *trans* ratio in vinylic systems is only seldom favored thermodynamically. The difference between the thermodynamic and kinetic *cis–trans* product ratios may be sometimes indicative for the intermediacy of **12**.

A saturated carbonium ion which is frontshielded by the leaving group tends to give racemization with an excess inversion by nucleophilic attack from the back side.[30] Differentiation between SN1 and SN2 reactions on stereochemical grounds is therefore difficult. In vinylic systems, when the leaving group is still in the plane of the vacant p orbital of **12**, attack from the other side with inversion is again favored. However, in bimolecular nucleophilic vinylic substitution of the "addition–elimination" type, the nucleophile attacks perpendicularly to the plane of the double bond and retention is usually observed.[31] Decision between this and the SN1 route is therefore possible on stereochemical grounds.

Retention by backshielding is the outcome of neighboring group participation in saturated systems and is also expected in the vinylic case.[32] Specific interaction of the leaving group with the *cis* or the *trans* substituents may give two different ion pairs. The stereochemistry would then be determined by their relative stabilities and interconversion rates compared to the solvolysis rates.

In the bent ion **13** the planar geometry ensures that attack from the back is sterically more difficult than from the front due to interference of *trans* groups and retention is predicted. The effect is strong enough so that it would probably dictate the stereochemistry even if ion pairs are formed. Formation of two "equilibrating bent ions" which equilibrate faster than they are captured by the solvent would give no steric or electronic gain. Although this is the case with vinylic radicals[33] the orbital involved contains one electron in the radical and is empty in the carbonium ion. The stereochemical predictions are summarized in Table IV.

Table IV. Stereochemical Predictions for Vinylic SN1 Reactions

Intermediate	Predicted stereochemistry
A. Linear Ion	
"Free" linear ion	"Racemization"
Frontshielded ion pair	Inversion
Two ion pairs with different stabilities	Generally unpredictable
Bridged ion	Retention
B. Bent Ion	
"Free" bent ion	Retention
Frontshielded ion pair	Preferred retention

Structure of the 1,2-Dianisyl-2-phenylvinyl Cation. The vinyl cation formed from three different precursors had been captured by seven nucleophiles in four different solvents. With two of these (water or hydroxide ion and the formate ion) **8** was formed and no conclusion could be drawn. The stereochemistry with alcohol (or ethoxide ion) was not determined. The two thio nucleophiles formed 1:1 *cis* to *trans* vinyl thiolates at the end of the reaction. Preisomerization of the bromides is too slow, while postisomerization of the thiolates is unlikely since the corresponding ethylenes do not isomerize at all under the reaction conditions. Moreover, the equilibrium mixture of the bromides and probably that of the thiolates is not 1:1 and this observed distribution is very likely kinetically controlled. With chloride ion the 1:1 ratio is also kinetically controlled since the bromide and the chloride isomerizations are slow and negligible, respectively, and the equilibrium mixture of the chlorides is not 1:1. Finally, in acetolysis in the presence of silver or sodium acetate the kinetically controlled ratio is 1:1 since product distributions are known when preisomerization is not extensive, while postisomerization is unimportant.

We conclude that *"racemization" is the stereochemical outcome of the SN1 solvolysis of 1,2-dianisyl-2-phenylvinyl halides* regardless of the stereochemistry of the starting material, the leaving group, the capturing nucleophile, and the solvent.

From the kinetic data in acetic acid[9] almost all the acetates and most of the organic chlorides are formed by capture of dissociated ions. In 80% ethanol products may be formed from dissociated ions which are captured faster than return, or more likely from "solvent-separated" ion pairs. The kinetic argument for SN1 reaction in the presence of thiolate ion was discussed for trianisylvinyl bromide[1] which reacts at a rate similar to that of **1** or **2**.[9]

Kinetic evidence in dimethylformamide is absent but analogy and the established SN1 mechanism in dimethylformamide[5d] suggest its operation for our system. The addition–elimination route for the apparently simi-

---

(30) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon," Elsevier Pub. Co., London, 1963, pp 88–93; D. Bethell and V. Gold, "Carbonium Ions," Academic Press, London, 1967, pp 174–177.

(31) Z. Rappoport, *Advan. Phys. Org. Chem.*, 7, 1 (1969).

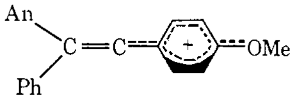
(32) If a neighboring group is capable of attacking perpendicularly, this would be a special case of the "addition–elimination" substitution route.

(33) J. A. Kampmeier and R. M. Fantazier, *J. Amer. Chem. Soc.*, **88**, 1959 (1966); R. M. Kopchik and J. A. Kampmeier, *ibid.*, **90**, 6733 (1968).

lar reaction of chloride ion with 1-anisyl-1-phenyl-2-chloroethylenes in dimethylformamide[15b] gives excess retention at higher temperature and our observed stereochemistry argues therefore for an SN1 process. Moreover, the bromides isomerize faster than they solvolyze in both acetic acid and dimethylformamide while the diarylchloroethylenes did not isomerize after 312 hr at 186°. The similar stereochemistry from reaction of both **1** and **2** is an additional argument to the kinetic one [1,9] against neighboring aryl participation.

Dissociated ions are the advanced intermediates along the ionization–dissociation pathway and therefore *dissociated α-anisyl-β,β-diarylvinyl cations in acetic acid, 80% ethanol, or dimethylformamide are linear, sp hybridized.* It is likely that the ions analogous to solvent-separated ion pairs in 80% ethanol have similar structures.

Maximum delocalization for our ion is achieved by allenic geometry at C_α as in **14**. Electrostatic repulsion by the π electrons may increase the lifetime of the cation by reducing the rate of approach of the nucleophile from the perpendicular direction.



14

Formation of 8. In 80% ethanol **8** is expected, but not in formic acid or in dimethylformamide. In formic acid, the solvolysis and the isomerization of the ethylenes may be an electrophilic addition–elimination as suggested for the solvolysis of vinyl tosylates.[34] Vinyl formates are easily cleaved to the ketones[7b] but since the ketone was obtained in a dry solvent before work-up the hydrolysis takes place in the solvolysis mixture. The mechanism of this cleavage needs additional work.

The ketone is formed in aqueous dimethylformamide[5b] but in our case the oxygen must come from the dry solvent. A possible intermediate is **15** which is hydrolyzed easily to **8**. Similar intermediates had been suggested in the formation of carbonium ions in dimethylformamide.[35]

$$Ar_2C{=}C(An){-}OCH{=}\overset{+}{N}Me_2$$

15

Experimental Section

Melting points are corrected. Nmr spectra were recorded with a Varian A56/60 spectrometer and the signal positions are given in cps downfield from internal tetramethylsilane. Mass spectra were recorded with an Atlas C4 instrument and uv on a Perkin-Elmer 450 spectrometer.

Solvents and Materials. 80% ethanol was prepared according to Grob.[5a] Basic solutions were prepared by dissolving analytical sodium hydroxide (Merck) in conductivity water and by addition of absolute alcohol to the required volume. Thiolate solutions were prepared by adding the calculated amount of thiol to an equimolar amount of sodium hydroxide in 80% ethanol. Acetic acid was prepared by refluxing analytical glacial acid (Baker) with 1% acetic anhydride, and distilling and collecting the middle fraction. Sodium acetate solutions were obtained by dissolving analytical grade sodium carbonate in acetic acid. Commercial silver acetate and lithium chloride were used. Formic acid was dried according to Conway.[36] Dimethylformamide was dried by azeotropic distillation with benzene and distillation from a preheated alumina. The "dry" solvent was refluxed for 2 days over either calcium hydride or Linde 4A molecular sieves and distilled.

1,2-Dianisyl-1-phenylethanol. Phenylmagnesium bromide (0.2 mol) in ether (70 ml) was added slowly to a suspension of desoxyanisoin (51.2 g, 0.2 mol) in a mixture of benzene (350 ml) and ether (175 ml) and refluxed for 2 hr. The mixture was poured into aqueous ammonia containing ammonium chloride, extracted with benzene, washed, dried, and the solvent was evaporated. Oil (55 g, 75%) was formed. A small sample was crystallized (ethanol) giving white crystals of 1,2-dianisyl-1-phenylethanol, mp 84–85°.

Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.82; H, 6.32. The sample showed the following characteristics: ir, OH stretching at 3570 cm^{-1}; nmr (hot CCl_4) broad 1 H singlet (OH) at 124.5 cps, 2 H singlet (CH_2) at 206 cps, 6 H two singlets (OMe), 219, 222 cps, 13 H multiplet (aromatic) 395–450 cps; mass spectra *m/e* 334 (0.3%, M), 317 (6%, M − OH), 316 (25% M − H_2O), 256 (6% M − C_6H_6) 135 (100% $AnCO^+$), 105 (30%, $PhCO^+$), 107 (18%, An), 77 (90%, Ph).

***cis*- and *trans*-1,2-Dianisyl-1-phenylethylene.** To the above mentioned oil (55 g), phosphoric acid (85%, 90 ml) was added and the mixture was kept at 90° for 3 hr, poured into a mixture of chloroform (100 ml) and ice–water (150 ml) and the aqueous layer extracted three times with chloroform (50 ml). The organic layer was washed, dried, and evaporated and the oil was crystallized from 80% ethanol–20% acetone. Oils were initially precipitated and separated by decantation, and recrystallized. After repeating this procedure twice, an isomer mixture, mp 65–75°, was formed and crystallized from a large volume of ethanol and left at room temperature. After a few days, a solid, mp 98–100°, precipitated and the filtrate gave after a few more days another fraction, mp 89–91°. Recrystallization of the first fraction (ethanol) gave *trans*-1,2-dianisyl-1-phenylethylene, mp 104.5–105.5° (lit.[37] 105.5–107°) and of the second fraction (ethanol) gave *cis*-1,2-dianisyl-1-phenylethylene, mp 93–94° (lit.[37] 92–94°).

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37. Found for the *cis* isomer: C, 83.35; H, 6.16. For the *trans* isomer: C, 83.71; H, 6.36. The fraction showed the following characteristics: ir (CS_2) peaks for both at 2840 (OMe) and 1610 (C═C) cm^{-1}. In the fingerprint region the different characteristic peaks are at 562, 753, and 802 cm^{-1} for the *trans* and at 576, 603, and 780 cm^{-1} for the *cis* isomer. Nmr data are given in Table II. The other peaks are similar to those of the carbinol. *m/e* 315 was not found.

1,2-Dianisyl-2-phenylvinyl Chlorides 10d and 11d. To a mixture of 1,2-dianisyl-1-phenylethylenes, mp 65–75° (8 g, 25 mmol), in carbon tetrachloride (30 ml), a solution of chlorine (1.75 g, 25 mmol) in carbon tetrachloride (40 ml) was added during 90 min, keeping the temperature at 40°. The solvent was evaporated and the oil was crystallized (cyclohexane). A solid, mp 94–100° (mainly **10d**), first precipitated. From the filtrate, and after standing for several hours, a white solid, mp 108–115° (mainly **11d**), precipitated. The total yield was 5.5 g (60%). The *cis* to *trans* ratio (by nmr) is 9:1. The first fraction was repeatedly crystallized (methanol) giving *cis*-1,2-dianisyl-2-phenylvinyl chloride **10d**, mp 109°.

Anal. Calcd for $C_{22}H_{19}ClO_2$: C, 75.34; H, 5.42; Cl, 10.11. Found: C, 75.53; H, 5.54; Cl, 10.50. The ir spectrum in the 3500–1500 cm^{-1} region is similar to that of the ethylenes. In the fingerprint region characteristic peaks are at 542, 560, *575*, 630, 700, 718, 746, *780*, 805, and 970 cm^{-1}. The italicized peaks can be used for differentiation from the *trans* isomer. Nmr (CCl_4) data included an aromatic to methoxyl proton ratio of 13:6; two methoxyl singlets at 219 and 221.5 cps (1:1); phenyl singlet (5H) at 427 cps; and an aromatic multiplet which separated into two quartets (protons at 394.5 and 410.5, and 399.5 and 432.5 cps). The second fraction was repeatedly crystallized (CCl_4) to a constant melting point, giving the *trans* isomer **11d**, mp 123–124°.

Anal. Calcd for $C_{22}H_{19}ClO_2$: C, 73.34; H, 5.42; Cl, 10.11. Found: C, 75.21; H, 5.36; Cl, 10.20.

The ir spectrum (CS_2) in the 3500–1500 cm^{-1} region is similar to that of the *cis* isomer. Important fingerprint peaks are: 545, 560, *625*, *635*, 700, 720, 749, *772*, 808, 970, 1042, 1180, 1255, and 1300 cm^{-1} (the italicized ones differ from those of the *cis* isomer). Nmr (CCl_4) spectra showed an aromatic to methoxyl proton ratio of 13:6; two methoxyls (1:1) at 222 and 226 cps; and an aromatic multiplet at 390–444 cps. The phenyl at *ca.* 419.5 cps appears as a broad doublet. Mass spectra are in Table III. Attempts to

---

(34) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968).

(35) A. F. Diaz and S. Winstein, *ibid.*, **86**, 5010 (1964).

(36) B. E. Conway and M. Dzieciuch, *Can. J. Chem.*, **41**, 21 (1963).

(37) K. Sisido, K. Okano, M. Sindo, and H. Nozaki, *J. Amer. Chem. Soc.*, **79**, 3591 (1957); E. C. Dodds, L. Goldberg, W. Lawson, and R. Robinson, *Proc. Roy. Soc.* (London), *Ser. B*, 127, 140 (1939). The geometrical structure was not assigned in these cases.

increase the ratio of the *trans* isomer by chlorination of pure *trans*-ethylene gave the same 9:1 ratio of **10d** to **11d**.

cis- **and** *trans*-**1,2-Dianisyl-2-phenylvinyl Bromide 1 and 2.** **a.** To a mixture of 1,2-dianisyl-1-phenylethylenes (6 g, 19 mmol) in carbon tetrachloride (30 ml), bromine (3 g, 19 mmol) was added during 15 min at ice-bath temperature. The bromine color was immediately discharged and hydrogen bromide evolved. The solvent was evaporated and the oil (7:3 ratio of **2**:**1**) was crystallized (cyclohexane) giving a solid, mp 100–109°, mainly the *cis* isomer. Repeated recrystallization (methanol) gave pale yellow monoclinic crystals of *cis*-1,2-dianisyl-2-phenylvinyl bromide **2**, mp 117°.

On standing, the mother liquor precipitates solids with higher percentages of the *trans* isomer. Mixtures with more than 50% *trans* isomer were crystallized (carbon tetrachloride) giving solids with *ca.* 80% *trans.* Repeated crystallization (methanol) to a constant melting point gave pale yellow monoclinic crystals of the *trans* isomer **1**, mp 135–136°. Seeding of the solution with one isomer results in preferential precipitation of this isomer. The total yield was 6 g (85%).

b. A mixture of ethylenes (25.3 g, 80 mmol) in carbon tetrachloride (400 ml) was refluxed for 90 min with N-bromosuccinimide (14.4 g, 80 mmol) and benzoyl peroxide (0.2 g) with irradiation with a sun lamp. The mixture was cooled to 0°, the succinimide filtered, the filtrate washed with water, dilute sodium hydroxide and water, and dried. Evaporation of the solvent gave oil (25 g, 90%) which had a 6:4 ratio of **2**:**1**. The isomers were separated as in **a** above.

Anal. Calcd for $C_{22}H_{19}BrO_2$: C, 66.83; H, 4.84; Br, 20.21. Found for the *cis* isomer: C, 66.61; H, 4.93; Br, 20.38. Found for the *trans* isomer: C, 66.73; H, 4.91; Br, 20.38.

The ir spectrum (CS_2) in the 3500–1500 cm^{-1} region is similar to that of the ethylenes. In the fingerprint region the peaks of the *trans* isomer are at 548, *615*, 625, 698, 715, 743, 768, 788, 797, 805, 830, 838, 960, 1040, 1113, 1180, 1240, and 1300 cm^{-1}. The *cis* isomer has peaks at 550, *575*, 628, 658, 710, 728, 740, 765, 778, and 803 cm^{-1}, the other peaks being similar to these in the *trans* isomer. The italicized peaks were used for differentiation. Other data are given in Tables I–III.

cis- **and** *trans*-**1,2-Dianisyl-2-phenylvinyl Acetate 10c and 11c.** A mixture of the vinyl bromides **1** and **2** (4.5 g, 11.5 mmol) was refluxed with silver acetate (1.95 g, 11.5 mmol) in glacial acetic acid (100 ml) for 90 min in a light-protected flask. The hot solution was filtered and evaporated, the oil formed extracted with carbon tetrachloride (100 ml), washed twice with water and sodium bicarbonate (100 ml), dried and filtered, and the solvent was evaporated. The oil (3.9 g, 92%) is a 1:1 mixture of the two isomers. Crystallization (CCl_4) gave a white solid, mp 115–130°, and from the mother liquor a solid, mp 105–120°, was separated. Repeated crystallization of the first fraction (CCl_4) gave 1 g (23%) of white crystals of *trans*-1,2-dianisyl-2-phenylvinyl acetate **11c**, mp 140–141°. Recrystallization of the second fraction (CCl_4 or methanol) gave first the *trans* isomer, mp 140°, and after separation of this, 850 mg (20%) of white crystals of the *cis* isomer **10c**, mp 117–118°. No attempt was made to increase yields by evaporation of the solution since purity of the isomers rather than quantity was desired.

Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found for the *trans* isomer: C, 77.23; H, 5.86. For the *cis* isomer: C, 76.81; H, 5.84. In the ir spectra (CS_2) both isomers show the C=O stretching absorption at 1770 cm^{-1}. The spectrum at 3500–1500 cm^{-1} is similar to that of the corresponding ethylenes. In the fingerprint region in the *trans* 520–530, 552, 573, 605, 700, 755, 780, *810*, and 830 cm^{-1} were exhibited and in the *cis* 525, 552, 575, 605, 700, 759, *798*, 810, and 830 cm^{-1} were shown. The italicized peaks are used for differentiation but they are too weak for a quantitative work. Nmr spectrum ($CDCl_3$) had for both isomers a ratio of the aromatic–methoxyl–methyl signals of 13:6:3; for the *trans* isomer, a singlet ($OCOCH_3$) at 114 cps, two equal singlets (OMe) at 222 and 225.5 cps, a singlet (Ph) at 423.5 cps and two overlappig quartets (protons at 395.5, 404.5, 421.5, and 425 cps); for the *cis* isomer, a singlet ($OCOCH_3$) at 111 cps, two overlapping singlets (OMe) at 220 and 220.5 cps; a singlet (Ph) at 430.5 cps and two merging quartets of the anisyl protons at 390–435 cps which were not analyzed. The mass spectra are given for the *trans* isomer only as *m/e*, relative abundance, and assignment of the ion: 374, 6%, M; 332, 17%, M − CH_2=C=O; 303, 17%, $An_2(Ph)C^+$; 197, 9%, $An(Ph)CH^+$; 135, 39%, $AnCO^+$; 107, 42.5%, An^+; 106, 32% $(An-H)^+$; 91, 39%, tropylium ion; 78, 49%, $C_6H_6^+$; 77, 100%, Ph^+; 43, 70%, CH_3CO^+.

10c and 11c from Pure Vinyl Halides. **a.** *trans*-1,2-Dianisyl-2-phenylvinyl bromide (475 mg, 1.2 mmol) and silver acetate (213 mg, 1.2 mmol) in acetic acid (40 ml) were refluxed for 1 hr. The oil obtained was treated as above and its nmr showed 1:1 singlets at 111 and 114 cps and 1770 cm^{-1} in the ir. Crystallization (CCl_4) gave a solid, 115 mg (25%), mp 129–132°, which was 1:9, **10c** to **11c** by nmr. The mother liquor is 3:1, **10c** to **11c**.

b. *cis*-1,2-Dianisyl-2-phenylvinyl bromide (95 mg, 0.24 mmol) and silver acetate (40 mg, 0.24 mmol) in acetic acid (10 ml) were refluxed for 45 min. The oil which was treated as above had an absorption at 1770 cm^{-1} and a 1:1 ratio of **10c** to **11c**.

c. *cis*-1,2-Dianisyl-2-phenylvinyl chloride (175 mg, 0.5 mmol) and silver acetate (80 mg, 0.5 mmol) in acetic acid (20 ml) were refluxed for 2 hr. The oil obtained which was treated as usual, showed absorption at 1770 cm^{-1} and 1:1 methyl singlets in the nmr. Crystallization (CCl_4) gave a solid, mp 126–130° which was 1:9, **10c** to **11c**. The other isomer was not isolated.

1,2-Dianisyl-2-phenylethanone 8. **a.** A mixture of 1,2-dianisyl-2-phenylvinyl bromide (4 g, 10 mmol) and silver fluoride (1.3 g, 10 mmol) in dry dimethylformamide was refluxed with stirring for 12 hr, the solvent was evaporated, and the oil formed was crystallized (methanol), mp 71–73° (1.5 g, 45%). Recrystallization (methanol) gave white 1,2-dianisyl-2-phenylethanone **8**, mp 75°.

Anal. Calcd for $C_{22}H_{20}O_2$: C, 79.50; H, 6.06. Found: C, 79.76; H, 5.86. Ir showed absorption (CS_2) C=O, at 1680 cm^{-1}; nmr (CCl_4) 1 H singlet (CH) at 346 cps, two 3 H singlets (OMe) at 217, 219.5 cps, 5 H singlet (Ph) at 426 cps and 8 H two quartets, J = 8.5 cps with protons at 467.5, 398 (An α to C=O) and 400, 419 (An β to C=O).

b. Reflux of **1** or **2** (90 mg, 0.22 mmol) in dimethylformamide (15 ml) for 36 hr, followed by evaporation of the solvent, extraction with carbon tetrachloride, washing, drying, and concentrating gave an oil with ir and nmr identical with those in **a** above.

c. In dry formic acid (20 ml) containing sodium formate (41 mg, 0.6 mmol) either **1** or **2** (158 mg, 0.4 mmol) was refluxed for 4 hr. The solvent was evaporated, the residue dissolved in carbon tetrachloride, washed with sodium bicarbonate and water, dried, and concentrated. Nmr and ir correspond to those of **8**. Crystallization of the residue before work-up (methanol or CCl_4) gave solids on cooling, but on filtration they became oils with ir and nmr of **8**. When the ir of the residue was taken immediately after evaporation of the solvent and before further work-up it corresponded to that of **8**.

Isomerization of the Ethylenes. Ratios of the ethylenes were determined by the relative integration of the nmr signals at 221.5 cps (*cis*) and 224.5 cps (*trans*). The sample was obtained by pouring the reaction mixture into water, extracting with carbon tetrachloride, drying and concentrating the organic layer.

a. Reflux of the *trans* ethylene (96 mg, 0.3 mmol) in formic acid (20 ml) for 48 hr, followed by the usual work-up gave a 1:1 ratio of the *cis* to *trans* ethylene.

b. Reaction of *cis* or *trans* ethylene (96 mg, 0.3 mmol) in basic (0.49 *N* sodium hydroxide) 80% ethanol (7 ml) at 120.3° for 64 hr, followed by the usual work-up showed no isomerization.

c. Reaction of *cis* or *trans* ethylene (96 mg, 0.3 mmol) in separate ampoules containing acetic acid (7 ml) and sodium acetate (49 mg, 0.6 mmol) at 120° gave after 5, 15, and 192 hr 24.5, 40 ± 1 and 100% isomerization of each ethylene. The calculation was based on the formation of an equilibrium mixture containing 59% *cis* and 41% *trans* ethylene as found. At 150°, the equilibrium mixture was obtained from the *cis* isomer after 18 hr.

Isomerization of the *trans* **Acetate.** **a.** Reaction of **11c** (110 mg, 0.3 mmol) for 46 hr at 120.3° in acetic acid (7 ml) containing sodium acetate (49 mg, 0.6 mmol) showed only the 114 cps signal and none of the 111 cps one. Isomerization is estimated to be less than 5%.

b. Tetrabutylammonium chloride (171 mg, 0.53 mmol) and **11c** (114 mg, 0.31 mmol) in acetic acid (7 ml) were kept for 150 hr at 150°. Titration and ir showed that no organic bromide was formed, and nmr showed less than 5% of the *cis* acetate.

Reactions in Acetic Acid. Reaction mixtures of vinyl halides with silver or sodium acetate in acetic acid were kept at the desired temperature, filtered (in runs with silver acetate), the acetic acid evaporated, the oil dissolved in carbon tetrachloride, washed with water and sodium bicarbonate, dried, and the solvent evaporated. Isomer distribution for each kinetic point was calculated from the relative integration of the 111 and 114 cps signals. For example, a 1:1 ratio of *cis* to *trans* acetate was obtained at 120.3° in reactions of 0.0435 mol/l. of vinyl halide and 0.087 mol/l. of sodium acetate at *ca.* 13, 23, 42, 61, 75, and 97% reaction for the two bromides and at 10, 20, and 36% reaction for the *cis*-chloride.

Reaction of 0.025 mol/l. of vinyl halide with an equimolar amount of silver acetate at reflux for 45–60 min, or at 80° for 30 min gave the same ratio. In experiments with excess vinyl halide, the unreacted vinyl halide was partially isomerized at the end of the reaction.

Reactions in 80% Ethanol. Reaction of 0.0435 mol/l. of *cis*- or *trans*-bromide in 0.39 *N* sodium hydroxide in 80% ethanol (7 ml) at 120° was followed titrimetrically. The half-life is about 45 min, and products were determined after 24 hr. After evaporation of the solvent, extraction with carbon tetrachloride, drying and concentrating, nmr showed the formation of the ketone **8** and ether **9** in a 3:1 ratio. Crystallization of the oil (methanol) gave a solid (10 mg, 15%) which depressed the mixture melting point with **8**, showed in the ir no sign for **1**, **2**, or **8**, and had C═C absorption at 1610 cm^{-1}. It was tentatively assigned as the ether **9**. On standing, the ketone **8** (30 mg, 50%) was separated and identified by ir, nmr, and mixture melting point.

The reactions of the vinyl halides (0.0435 mol/l.) and *p*-toluenethiolate and benzylthiolate ions (0.087 mol/l.) were conducted in ampoules at 120° At the end of the reaction the solvent was evaporated, the residue dissolved in carbon tetrachloride and washed with 5% sodium hydroxide, but traces of the free thiol were, however, always present. Analysis of the product by nmr was discussed.

Reactions in Dimethylformamide. In reactions in dimethylformamide the solvent was evaporated at the end of the reaction, the oil dissolved in carbon tetrachloride, washed with water, and the organic layer dried and evaporated.

Reaction of **1** (90 mg, 0.3 mmol) in dimethylformamide (20 ml) for 80 hr at reflux showed that 10% of **1** still remained. The only product formed was the ketone **8** (nmr). In dimethylformamide containing 3% water, **1** disappeared completely after 40 hr.

Reaction of **2** (90 mg, 0.3 mmol) in dimethylformamide (20 ml) gave after 31 and 40 hr, 24 and 30%, respectively, of **1**, while 64 and 70% of **2** were formed from **1** after 22.5 and 30 hr. The accompanying product was **8**.

Reactions with Lithium Chloride. Quantitative separation between the chlorides and the bromides by vpc or tlc were unsuccessful. The disappearance of the bromide was therefore followed by the ir peaks at 575 (for the *cis*), 615 (for the *trans*) and 960 cm^{-1} (for both bromides). The formation of the chloride was followed by the 635 cm^{-1} peak of the *trans*-chloride and the 970 cm^{-1} peak which is common to both chlorides. The chloride-bromide ratio was determined from the intensities of the 960 and 970 cm^{-1} peaks. The 575 cm^{-1} peak is common for both the *cis* chloride and bromide and additional quantitative determination was by integration of the methoxy signals in the nmr. The error in the combination of the method may be as high as 10%.

a. Lithium chloride (750 mg, 18 mmol) and **1** (350 mg, 0.89 mmol) were refluxed in dimethylformamide (70 ml) for 136 hr. The oil showed formation of a 1:1 ratio of chlorides and was crystallized from methanol. A solid, mp 120–121° (40 mg, 13%), was precipitated and identified as *trans*-chloride **11d** by analysis, ir, and mixture melting point. After few hours, another fraction (20 mg, 6.5%) was precipitated and shown by ir to be a 6:4 ratio of **10d** to **11d**. No attempt was made to isolate more material.

b. Lithium chloride (435 mg, 10.5 mmol) and **2** (200 mg, 0.5 mmol) were refluxed in dimethylformamide (50 ml) for 136 hr. The oil contained a 1:1 ratio of chlorides and crystallized from methanol. On a few days standing pure **11d**, mp 120–121° (25 mg, 14%), was obtained and identified by ir and mixture melting point.

c. Lithium chloride (23 mg, 0.55 mmol) and **1** (120 mg, 0.3 mmol) were refluxed in acetic acid (7 ml) containing sodium acetate (6 mg, 0.08 mmol) at 120.3° for 280 min. The ir showed the formation of 50% chlorides which were in a 1:1 ratio of *cis* to *trans* and the remaining 50% bromides were in a 4:6 ratio of *cis* to *trans*.

Meisenheimer-Type Compounds from Heteroaromatic Substrates. The Reaction of Methoxide Ion with 3,5-Dinitro-4-methoxypyridine in Methanol Solution[1]

Paola Bemporad, Gabriello Illuminati, and Franco Stegel

Contribution from the Department of Chemistry, University of Rome, 00185 Rome, Italy, and Centro C.N.R. (Rome) dei Meccanismi di Reazione.

Received April 3, 1969

Abstract: The formation and isolation of sodium 4-aza-1,1-dimethoxy-2,6-dinitrocyclohexadienate (adduct III) as resulting from the action of CH_3ONa on 3,5-dinitro-4-methoxypyridine in methanol solution are described. The structure of the adduct was proved by spectral evidence (nmr, uv and visible, and ir). The equilibrium constant and the rate of formation have been determined and compared with similar data for the trinitro analog I. The implications of the present results on the influence of aza activation on the mechanism of nucleophilic aromatic substitution are discussed.

In recent studies on nucleophilic heteroaromatic substitution[2] the physical organic aspects of aza activation have been contrasted with those of nitro activation. In several instances the effect of the aza group on reactivity is similar to that of the nitro group; but relevant differences also exist, such as the lower steric requirements of the aza group and its relatively important H-bonding interactions with the medium.[3] With regard to the reaction mechanism, a two-stage process *via* the formation of an intermediate σ complex is well established in the case of nitro activated aromatics.[4] A main piece of evidence in support of this hypothesis is the actual detection and isolation of the Meisenheimer compounds,[5] *i.e.*, the adducts formed from picryl ethers and alkoxides. In recent years, typical Meisenheimer compounds, such as I, have been intensively investigated in view of their theoretical importance as reaction intermediates; the subject has been reviewed recently.[6,7]

---

[1] Nucleophilic Heteroaromatic Substitution. XXXI.

[2] G. Illuminati, *Advan. Heteroc. Chem.*, 3, 285 (1964).

[3] G. Illuminati, G. Marino, and G. Sleiter, *J. Amer. Chem. Soc.*, 89, 3510 (1967); F. Genel, G. Illuminati, and G. Marino, *ibid.*, 89, 3516 (1967); M. Calligaris, G. Illuminati, and G. Marino, *ibid.*, 89, 3518 (1967).

[4] J. F. Bunnett, *Quart. Rev.* (London), 12, 1 (1958); S. D. Ross, *Progr. Phys. Org. Chem.*, 1, 31 (1963).

[5] In this and subsequent papers of the series the terms "Meisenheimer compound" and "adduct" are referred, for convenience, to the cyclohexadienate ion derivative, *i.e.*, to the anionic part of the Meisenheimer-like salt.

[6] R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, 16, 61 (1966).

[7] E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev.* (London), 22, 123 (1968).