Solvent Effects in the Conversion of Phenyldiazomethane into Stilbene and Spirooxetane in the Reaction with Chloranil

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A stereochemical study was made of the reaction of phenyldiazomethane(**1**) with chloranil(**2**) at 20 °C in 28 aprotic solvents. The products were *trans*-spirooxetane(**4**) and *cis-trans* mixtures of stilbene(**3**) (*ca.* 2—5 times *cis*-rich). The molar ratios of *cis*-**3** to the sum of the *trans*-**3** and **4** tended to increase, whereas the **4** to *trans*-**3** ratios decrease with the increase in the solvent basicity and polarity. These effects of solvents on the product distributions were interpreted in terms of the effects of the solvent basicity and polarity on the stereoselective formation of the diazonium betaine intermediate and on the conformational isomerism. Moderately successful linear-free-energy(LFE) relationships were established for these product ratios with the aid of the combination of the empirical solvent basicity parameter, D_π, and the Kirkwood function, $f(\varepsilon)$, or E_T values as the solvent polarity parameters.

Our recent studies have shown that the decomposition of phenyldiazomethane (**1**) and its substituted homologs with chloranil(**2**) gives *trans*-spirooxetanes and stilbenes.[1] The stereochemistry of these products was 100% *trans* for spirooxetanes and *cis*-isomer-rich for stilbenes: the *cis*:*trans* ratios of the stilbenes increased with the electron withdrawal of the substituents. The preliminary solvent effects showed that THF brings about higher *cis*:*trans* ratios of stilbenes and lower relative yields of spirooxetanes than 1,2-dichloroethane. We have now extended the work to various aprotic solvents. Thus, the present paper is aimed to make a more penetrating interpretation of the effects of solvents on the stereochemical phenomena and on the product distributions. For this purpose, the use of the linear correlations with solvent basicity and the polarity parameters was examined.

Results and Discussion

As was described in a previous paper,[1] the formation of stilbene (**3**) and *trans*-spirooxetane(**4**) can be well explained by postulating two diazonium betaine intermediates, I and II (Scheme 1). II may be produced by a nucleophilic attack of **1** on I. II is degradated to **3** *via* the elimination of N_2 and **2** (Path a) or to **4** *via* the intramolecular cyclization (Path b). The reaction of **1** with **2** also gave several by-products resulting from the nucleophilic attack of residual water on I.[1]

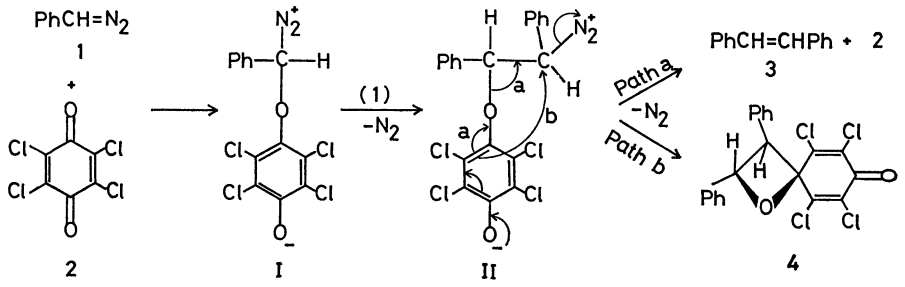
Our attention in the present study was restricted to the solvent effects in the stereochemical pathway leading to **3** and **4**; thus, the only efforts to determine the distribution of *cis*-, *trans*-**3** and **4** were made by the use of high-performance liquid chromatography. The results in a wide variety of aprotic solvents are tabulated in Table 1.

It is noteworthy that the thermodynamically less stable *cis*-**3** was preferentially formed, *ca.* 2 to 5 times more than *trans*-**3**. The isomer ratios of **3** were high in acyclic ethers, such as diethyl ether and dipropyl ether, but considerably decreased in nitro compounds and nitriles. However, **4** was found to be a stable *trans*-isomer in any solvent, and its relative yields increased in the nonpolar solvents, such as benzene and carbon tetrachloride.

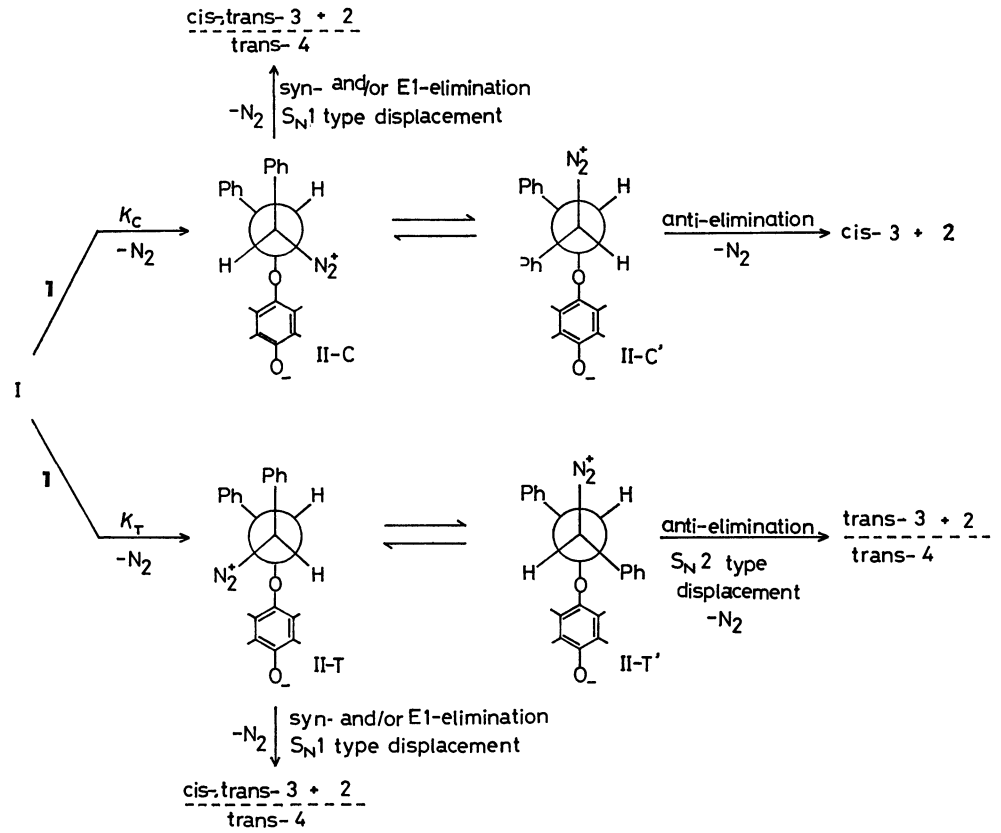
Table 1, Product distributions on the reaction of phenyldiazomethane(**1**) with chloranil(**2**) in various aprotic solvents

	Solvent	Relative yields[a]	
		3(*cis*/*trans*)	**4**
1	Diethyl ether	67.7(5.01)	32.3
2	Dibutyl ether	65.3(4.89)	34.7
3	Dipropyl ether	66.7(4.75)	33.3
4	Carbon tetrachloride	57.7(4.55)	42.3
5	Dimethoxymethane	69.6(4.46)	30.4
6	Tetrahydropyran	78.4(4.32)	21.6
7	Cyclohexanone	86.2(4.03)	13.8
8	Butyl acetate	83.2(3.97)	16.8
9	1,4-Dioxane	70.9(3.94)	29.1
10	1,2-Dimethoxyethane	81.9(3.89)	18.1
11	Tetrahydrofuran	78.9(3.77)[b]	21.1
12	Benzene	60.3(3.70)	39.7
13	Chloroform	59.4(3.65)	40.6
14	Methyl acetate	81.1(3.53)	18.9
15	Isopropyl acetate	79.4(3.45)	20.6
16	Ethyl methyl ketone	87.1(3.40)	12.9
17	1,1-Dichloroethane	63.9(3.39)	36.1
18	1,2-Dichloroethane	61.6(3.34)[b]	38.4
19	Propyl acetate	77.8(3.16)	22.2
20	Nitrobenzene	78.7(3.08)	21.3
21	Butyronitrile	82.3(2.97)	17.7
22	Propionitrile	77.7(2.96)	22.3
23	Acetone	82.9(2.89)	17.1
24	Dichloromethane	59.4(2.88)	40.6
25	Ethyl acetate	81.3(2.71)	18.7
26	Benzonitrile	71.1(2.31)	28.9
27	Acetonitrile	78.2(2.23)	21.8
28	Nitromethane	72.6(1.92)	27.4

a) The total yields of **3** and **4** exceeded 50% in most cases. b) The present values, determined by high-performance liquid chromatographic analyses, are somewhat different from the data obtained by a usual column chromatographic separation method and NMR measurements, probably because of the degradation of **4** into *trans*-**3** and **2** in the previous column-chromatographic treatment.



Scheme 1.



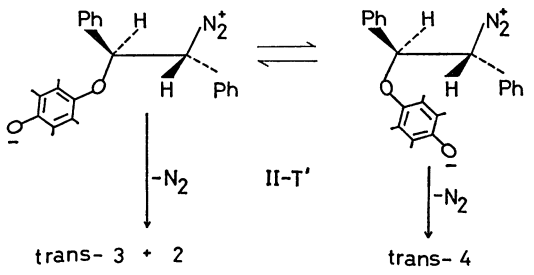
Scheme 2.

Conformational Analysis. As was shown in our previous paper,[1] two conformers, II-C and II-T, may be depicted as the most stable ones for the resulting threo and erythro stereoisomers of II respectively, as may be seen in Scheme 2. From the sterical point of view, II-C is slightly more stable than II-T; *i.e.*, the formation of II-C is a lower-energy process than that of II-T($k_C > k_T$). These conformers, II-C and II-T, can be in equilibrium with each other with the respective conformational isomers, II-C′ and II-T′. On grounds of both the steric and electronic factors, the populations of these threo and erythro rotamers are thought to be in the order of II-C>II-C′, and II-T>II-T′, II-C′ being the most unstable rotamer. The more populous II-C and II-T will afford *cis-trans* mixtures of **3** *via* the syn- and/or *E*1-type elimination, and *trans*-**4** *via* the intramolecular S_N1-type displacement. On the other hand, the less populous II-C′ will prefer to give *cis*-**3** *via* the anti-elimination. II-T′ will prefer to give *trans*-**3** *via* the anti-elimination and *trans*-**4** *via* the intramolecular S_N2-type displacement (Scheme 2).

It should also be noted here that the S_N2-type displacement giving *trans*-**4** is only possible when the bent-ether linkage of these rotamers can be aligned so as to build up a four-membered ring with the central C–C bond, as is represented in the conformational equilibrium of II-T′ (Scheme 3). However, II-C′ will not be transformed into such a crowded structure because of the unfavorable phenyl-phenyl *cis* repulsion. This steric repulsion is the reason why *cis*-**4** was not formed in the present reaction.

Most of the solvents provide a higher yield of *cis*-**3** than the sum of *trans*-**3** and **4**. This apparently means that the reactions from II-C′ and II-T′ proceed more rapidly than those from II-C and II-T.

Solvent Effects on the cis- *to* trans-*Products Ratios.* In the nucleophilic attack of **1**, basic and polar sol-



Scheme 3.

vents tend to stabilize the cation center of I, and thereby appear to suppress its reactivity. As a guiding principle of chemical behavior, the reactivity-selectivity principle(RSP)[2] suggests that the less reactive the diazonium betaine, I, the more stereoselective will be the attack of **1**. Assuming that most of the **3** and **4** arise from the II-C′ and II-T′ conformers, as has been mentioned above, the molar ratios of *cis*-**3** to the sum of *trans*-**3** and **4** may be said to be approximately parallel to the rate ratio(k_C/k_T).

Keeping these considerations in mind, we preliminarily attempted to correlate the logarithms of the molar ratios of *cis*-**3** to the sum of *trans*-**3** and **4** with such empirical solvent-basicity parameters as D_π,[3] Kagiya's $\Delta\nu_D$,[4] Gutmann's *DN*,[5] and Kamlet-Taft's β.[6]

When correlated with these conventional parameters, the regression equations are as follows: log *cis*-**3**/(*trans*-**3**+**4**) $= 0.142+0.149D_\pi$($r=0.782$, $n=24$), $=-0.00512+0.0027\Delta\nu_D$($r=0.731$, $n=22$), $=-0.0337+0.0115DN$ ($r=0.808$, $n=14$), and $=-0.142+0.698\beta$ ($r=0.727$, $n=13$), where r and n are the correlation coefficients and the number of data points respectively. However, the correlations with the solvent-polarity parameters, *i.e.*, the Kirkwood function[7] of dielectric constants ε, $f(\varepsilon)=(\varepsilon-1)/(2\varepsilon+1)$ and Dimroth and Reichart's E_T values,[8] provided worse results for $f(\varepsilon)$, ($r=0.156$, $n=23$) and for E_T, ($r=0.102$, $n=20$). Thus, the specific role of the solvent basicity is much more important than its polarity effects. These statistical results are substantially in accordance with the above assumption that the further stereoselective formation of II-C is achieved by the nucleophilic solvation of the cation of I. The better correlation with D_π than with $\Delta\nu_D$ or β is suggestive of a soft acidity of the cation center(N_2^+) of I, because the indicator compounds employed for the determination of D_π and $\Delta\nu_D$ or β are typical soft-acid TCNE and hard-acid methanol or phenol respectively.[9] Though D_π is a slightly less successful parameter than *DN*, the ten more available values for D_π force us to adopt this parameter in the present discussion.

The more basic and the more polar the solvents are, the easier the conformational rotation into II-C′ and II-T′ will be. Thus, II-C′ and II-T′ play a much more significant role in the product distributions, ultimately increasing the net amount of *cis*-**3**. Therefore, we attempted to improve the above unsatisfactory correlation by the use of two parameters, D_π and the polarity parameter, $f(\varepsilon)$ or E_T. Equations 1 and 2

$$\log\frac{cis\text{-}3}{trans\text{-}3+4} = -0.105 + 0.169D_\pi + 0.632f(\varepsilon) \quad (r=0.863,\ s=0.0684,\ n=23) \quad (1)$$

$$\log\frac{cis\text{-}3}{trans\text{-}3+4} = -0.0957 + 0.155D_\pi + 0.00589E_T \quad (r=0.801,\ s=0.0801,\ n=20) \quad (2)$$

were obtained for the D_π-$f(\varepsilon)$ and D_π-E_T systems respectively. The positive coefficients of both D_π and $f(\varepsilon)$ or E_T are in harmony with the hypothesis that the solvent with a more basic and polar nature induces a more stereoselective formation of II-C than II-T and promotes the conformational transformation into II-C′ and II-T′. A plot of log *cis*-**3**/(*trans*-**3**+**4**) (obsd) *versus* log *cis*-**3**/(*trans*-**3**+**4**)(calcd) according to Eq. 1 is shown in Fig. 1. It is noticeable that nonpolar solvents, such as benzene and carbon tetrachloride, afforded exceptionally lower *cis*-**3** values with respect to the *trans*-products; *i.e.*, the logarithmic ratios were below null. These phenomena may be attributed to the more significant participation of the minor syn- and/or *E*1-type elimination and S_N1-type displacement, most probably from II-C. The reason for this may be that the conformational rotation into II-C′ is energetically more costly compared to the corresponding transformation of II-T into II-T′.

*Solvent Effects on the Spirooxetane(**4**) to* trans-*Stilbene (**3**) Ratios.* It is also interesting to examine the solvent effects on the competitive S_N2-type and anti-elimination processes, giving **4** and *trans*-**3**, from II-T′, because the solvent-dependent equilibrium situation between the extended and the crowded structures, as represented in Scheme 3, plays a significant role in these product ratios. The more basic and more polar solvents are liable to separate the opposite charges of II-T′, so that the amount of **4** decreases as a result of the reduced contribution of the crowded structure. On the other hand, in the less basic and

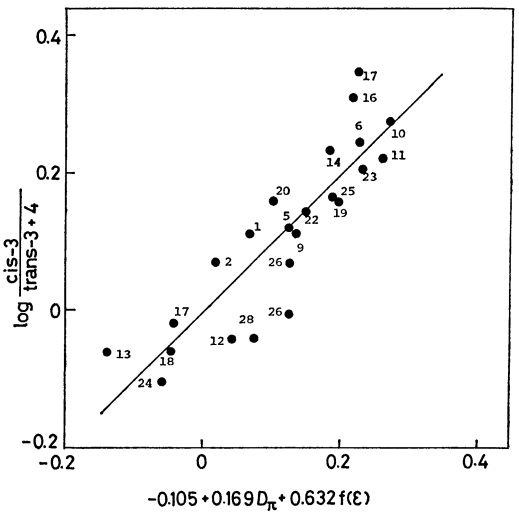


Fig. 1. Plot of $\log\frac{cis\text{-}3}{trans\text{-}3+4}$ (obsd) *versus* $\log\frac{cis\text{-}3}{trans\text{-}3+4}$ (calcd) according to Eq. 1; for point numbers, see Table 1.

less polar solvents the opposed charges should come close together; thus, the growing participation of the crowded structure increases the formation of **4**. A similar type of solvent contribution to product distributions can be expected for the minor S_N1- and/or $E1$-type elimination processes. In consideration of this, we attempted to correlate the logarithms of the molar ratios of **4** to *trans*-**3** with the linear combination of two parameters, D_π and $f(\varepsilon)$ or E_T. Equations 3 and 4 were thus obtained:

$$\log\frac{\mathbf{4}}{\textit{trans}\text{-}\mathbf{3}} = 1.07 - 0.232D_\pi - 2.37f(\varepsilon)$$
$$(r=0.921,\ s=0.0937,\ n=23), \quad (3)$$

$$\log\frac{\mathbf{4}}{\textit{trans}\text{-}\mathbf{3}} = 2.16 - 0.259D_\pi - 0.0514E_T$$
$$(r=0.930,\ s=0.0883,\ n=20). \quad (4)$$

The negative coefficients in both the basicity and the polarity parameters are consistent with the solvation environment expected above.

A comparison of the coefficients in Eqs. 1 and 2 with those in Eqs. 3 and 4 shows that the effects of the solvent basicity are more enhanced in log *cis*-**3**/(*trans*-**3**+**4**) than in log **4**/*trans*-**3**. The reverse is necessarily true for the contribution of the solvent polarity. A plot of log **4**/*trans*-**3**(obsd) *versus* log **4**/*trans*-**3**(calcd) according to Eq. 4 is shown in Fig. 2.

This figure consists of two solvent groups except for 1,4-dioxane. One group on the high side contains aliphatic chlorinated solvents (very low D_π and moderate high E_T) and acyclic ethers and benzene (moderate high D_π and very low E_T). Therefore, the high **4**:*trans*-**3** ratios can be ascribed to the low D_π or E_T values; that is, these solvents can not well stabilize the cation or anion center of II, increasing the population of the crowded structures. On the other hand, the other group on the low side is characterized by such solvent properties as a relatively strong nucleophilicity(high D_π) and/or electrophilicity

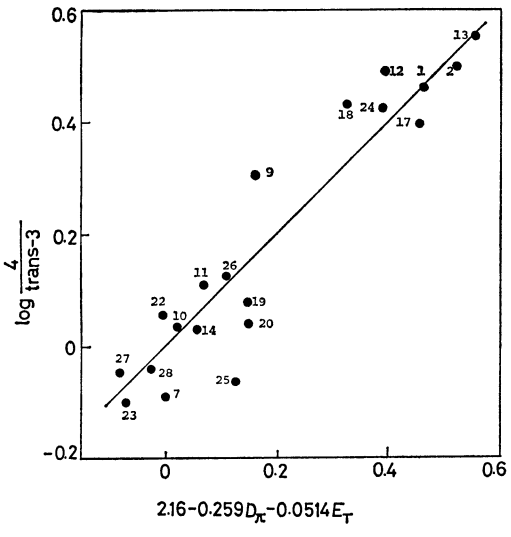


Fig. 2. Plot of $\log\frac{\mathbf{4}}{\textit{trans}\text{-}\mathbf{3}}$ (obsd) *versus* $\log\frac{\mathbf{4}}{\textit{trans}\text{-}\mathbf{3}}$ (calcd) according to Eq. 4; for point numbers, see Table 1.

(high E_T). Thus, the ketones, such as acetone and cyclohexanone, reduce the **4**: *trans*-**3** ratios much more because of both the effective nucleophilic and electrophilic solvations of the respective cation N_2^+ and anion chloranil moieties of II, consequently decreasing the population of the crowded structures. Though the esters have D_π values very close to those of ketones, the **4**:*trans*-**3** ratios appreciably increased on account of the slight decrease in E_T values. Similarly, though the E_T values for nitro compounds and nitriles are higher than those for ketones, the less basic properties (lower D_π) of these solvents induce more formation of **4**.

Experimental

The *cis*:*trans* ratio of **3** and the overall yields of **3** and **4** were determined by means of JASCO tri-rotor high-performance liquid chromatography (HPLC), using naphthalene as the internal standard. The HPLC analysis was carried out at room temperature using a 250 mm×4.6 mm column packed ODS (octadecyl silane on silica gel; methanol–water(4:1 by volume); flow rate, 1—1.5 ml/min. The UV detector was calibrated at 280 nm with standard mixtures of known concentrations of *cis*- and *trans*-**3** and **4**. The average error in the *cis*:*trans* ratio was *ca.* 3% or better. The relative retention times were as follows: naphthalene (1.0), *cis*-**3**(1.8), *trans*-**3**(2.3), and **4**(4.5).

Materials. The phenyldiazomethane(**1**) was prepared according to the procedure described by Closs and Moss[10] and was used without further purification. The chloranil (**2**) was of commercial origin and was recrystallized from benzene. All the solvents used were purified by the usual method.[11]

General Procedure. To a solution or suspension of **2** (0.50 g, 2.03 mmol) in a solvent (30 ml) was added, drop by drop, a solution of **1** (0.50 g, 4.24 mmol) in the same solvent(10 ml) for 10 min at 20 °C. The deep-red color of the mixture rapidly disappeared with a violent evolution of N_2. After 1-h stirring, the solvents (except for benzene) boiling below 100 °C were evaporated, and the pasty residue was redissolved in benzene (40 ml). In the case of the higher-boiling solvents, the reaction solutions were submitted to the following treatment without any work-up. In these reaction solutions, naphthalene(100 mg) was dissolved as an internal standard and two-milliliter aliquots were diluted with benzene until the total volume of solution rose to 25 ml. The sample solutions thus prepared were analyzed by HPLC.

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