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Stereochemistry in the Conversion of Phenyldiazomethane into Stilbenes and Spirooxetanes Caused by Tetrahalogenated 1,4-Benzoquinones. Effects of Halogen Substituents

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Synopsis. Reaction of phenyldiazomethane (**1**) with tetrafluoro-1,4-benzoquinone (**2a**) gave isomeric mixtures of stilbenes (**3**, cis/trans=4.7) and spirooxetanes (**4a**, cis/trans=1.1) via zwitterion intermediates. Similarly, tetrabromo-1,4-benzoquinone (**2c**) provided **3** and spirooxetane (**4c**); however, the cis/trans ratio of **3** dropped to 2.3 and **4c** was solely the trans isomer. On the other hand, reaction with tetraiodo-1,4-benzoquinone (**2d**) afforded no spirooxetane and gave a further reduced isomer ratio of **3** of 1.9.

Phenyldiazomethanes are reported to give *cis*-stilbenes in preference to their more stable trans-isomers on the metal salt-catalyzed decomposition by cerium(IV) ammonium nitrate,[1] copper(II) perchlorate and bromide,[2] lithium bromide,[3] and rhodium(II) acetate and iodorhodium(III) tetraphenylporphyrin,[4] and by photosensitized and anodic oxidation.[5] These stereoselective reactions can be explained by several alternative mechanisms; (1) carbene formation accompanied by the stereocontrolled attack of the second molecule of diazoalkanes,[2,4] (2) highly ordered alignment of two molecules of phenyldiazomethanes by sandwiching of two lithium ions with the π-electron system of diazoalkanes,[3] (3) face-to-face interaction performed by orbital mixing between the HOMO of the phenyldiazomethanes and the LUMO of their corresponding radical cations.[5]

We also observed formation of *cis*-stilbene over trans-isomer together with *trans*-spirooxetane from the reaction of tetrachloro-1,4-benzoquinone (**2b**) with phenyldiazomethane (**1**).[6] We have now extended the work to a series of tetrahalogenated quinones (tetrafluoro-, tetrabromo-, and tetraiodo-1,4-benzoquinones, **2a**, **2c**, and **2d**) to gain a better understanding of steric and electronic effects in the stereochemical course of the reactions.

Results and Discussion

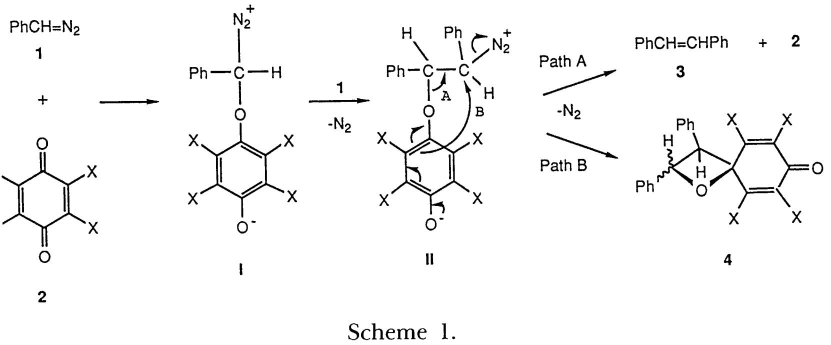
Reaction of 2 equiv of phenyldiazomethane (**1**) with quinones **2a**, **2c**, and **2d** at 20 °C in 1,2-dichloroethane proceeded to give stilbenes (**3**) and spirooxetanes (**4**) (Scheme 1). The results are summarized in Table 1 together with the previous data for **2b**.[6a] As noted, **3** predominated over **4** in all the cases and the relative yields of **3** to **4** increased in the order of **2a**<**2b**<**2c**<**2d**. The cis : trans isomer ratios of **3** well exceeded unity but gradually decreased from 4.7 to 1.9 with the increasing bulk of quinones. For **4**, quinone **2a** provided a slight excess of cis-isomer, whereas quinones **2b** and **2c** furnished solely trans-isomers and the most voluminous **2d** gave no **4**.

As previously described, formation of **3** and **4** can be rationalized by the reaction sequence involving generation of 1 : 1 zwitterion intermediates (**I**), addition of the second molecule of **1** giving 1 : 2 zwitterion (**II**), and product-determining elimination of N_2 and quinone (Path A) and cyclization (Path B), respectively (Scheme 1). Possible reasons why path A yields more *cis*-**3** than *trans*-**3** can be attributable to: (1) addition of **1** to **I** controlled by conformer steric effects as well as electronic attraction of the positive diazonium and negative quinone functions, thus the resulting threomer **II-C** being more preferred than erythromer **II-T**, (2) conformational rotation of **II-C** and **II-T** to **II-C′** and **II-T′**, respectively, and (3) anti-elimination of

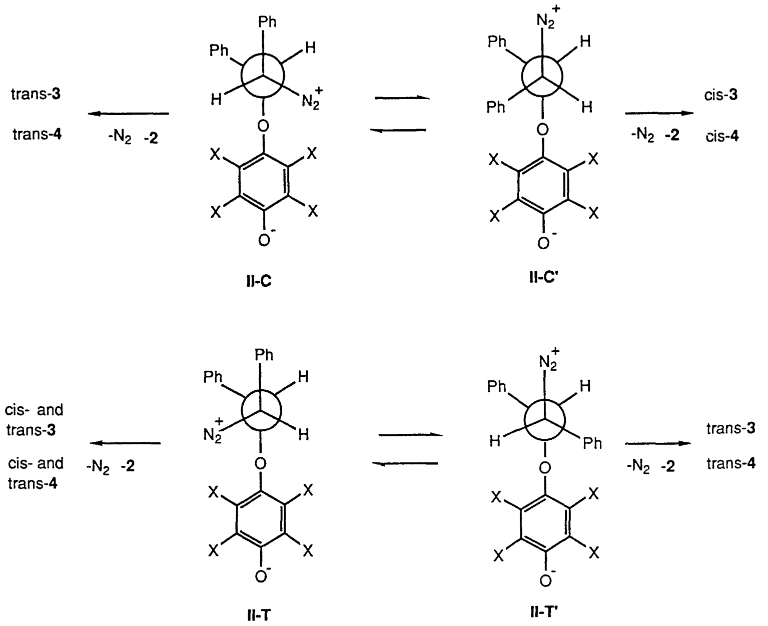
Table 1. Reaction of Phenyldiazomethane (**1**) with Tetrahalogenated 1,4-Benzoquinones (**2a**—**d**)[a]

Quinone	Products yields/%[b,c]		
	Relative		Total
	3 (cis/trans)	**4** (cis/trans)	
2a	59 (4.7)	41 (1.1)	81
2b	62 (3.3)[d]	38 (0)[d]	76
2c	74 (2.3)	26 (0)	58
2d	100 (1.9)	0	51

a) Carried out by addition of 2 equiv of **1** relative to quinones **2**. b) Determined by HPLC analysis. c) Based on **1** used. d) From Ref. 6c.



Scheme 1.



Scheme 2.

Table 2. Photoaddition of *cis*- and *trans*-Stilbene (**3**) with Equimolar Quinones **2a**—**d**

Quinone	Stilbene	Concentration mmol dm^{-3}	Reaction time/h	Oxetane (**4**) Yield/% (cis/trans)
2a	cis	80	4	16 (0.10)a)
2a	trans	80	4	17 (0.06)a)
2b	cis	50	3	78 (0)b)
2b	trans	50	3	79 (0)b)
2c	cis	70	3	54 (0)c)
2c	trans	70	3	61 (0)a)
2d	trans	30	4	0

a) Determined by HPLC. b) From Ref. 6b. c) Analyzed by NMR.

nitrogen and quinone (Scheme 2). The more populous **II-C** leads to *cis*-**3** and *cis*-**4** and the less populous **II-T** to *trans*-**3** and *trans*-**4**. El-type elimination from **II-C** and **II-T** must be taken into consideration because of exceptionally labile leaving group of N_2. Such prior loss of N_2 is expected to afford the stable *trans*-**3** and *trans*-**4** for **II-C** and isomeric mixtures of **3** and **4** for **II-T** in view of the conformational arrangements as well as the apparent release of rotational strain.

The decreasing tendency to produce **4** with increasing bulkiness of halogen atoms (F→I) can be interpreted by the increasing steric hindrance for the cyclization of intermediates **II** and **II′** compared to unstrained olefin formation. Such steric repulsive effect is also reflected on the stereochemistry of formed **4**; the smallest F substituents permitted the slightly excess formation of less stable *cis*-**4a** from the conformer **II-C′**, however, bulkier Cl and Br substituents could not allow cis-isomers and the bulkiest I substituents even stable trans-isomer. In accordance with these steric considerations, photochemical (2+2) cycloaddition of quinones **2a**—**d** with *cis*- and *trans*-**3** was found to give a mixture of *cis*- and *trans*-**4a** for **2a** and only *trans*-**4b,c** for **2b** and **2c**. Here, again, iodo-substituted **2d** was not able to take part in this photocyclization (Table 2). It is noticeable that **4** were photochemically produced in essentially the same yields and the comparable isomer ratio in spite of the geometrical difference of starting **3**, though the cis/trans ratio (=0.06—0.10) of **4a** drastically dropped when compared with the reaction with **1**. This observation may be due to fast rotation around the central C–C bond of biradical intermediate6b) and the photoisomerization of **3**. In fact, unreacted **3** showed considerable stereorandomization (cis/trans≈1.1) on **4** hours of irradiation in the presence of quinone **2a**.

The decreasing cis : trans ratios of **3** in going from **2a** to **2d** can be attributed to the significantly increasing conformational barrier of the main route (**II-C**→**II-C′**) for *cis*-**3**, since this rotation includes clearly the large torsional energy associated with eclipsing of two phenyl groups. Accordingly, the population of **II-C′** appears to be lowered with the bulk of halogens and the leak from the preferred conformer **II-C** to *trans*-**3** and *trans*-**4** will become appreciable.

Experimental

The IR, NMR, UV, and mass spectra were taken on a Perkin Elmer 983G, a Varian EM 390, a JASCO UVIDEC-505, and a JEOL JMS-DX 303 HF spectrometers, respectively. HPLC was made by using a Hitachi 655A-12 pump, a 655A UV monitor, and a D-2000 chromato integrator. The HPLC conditions using a Waters radial pak cartridge (8MBC18 10 μ; 8×100 mm) are as follows: eluents, 20 and 25% aqueous methanol (v/v); flow rate, 1 ml min^{-1} UV detector, 280 nm.

Materials. The 1,2-dichloroethane was refluxed over phosphorus pentaoxide and fractionated. Phenyldiazomethane was synthesized just before use according to the method of Closs and Moss.[7] Commercially available quinone **2a** was chromatographed through silica gel with 30% hexane-benzene (v/v) and then recrystallized from a mixture of hexane and benzene; mp 175—176 °C. Quinones **2c** and **2d** were prepared by the literature procedure[8] and were purified by recrystallization; mp 295 °C (from benzene) and mp 276 °C (from ethyl acetate), respectively.

Reaction with Tetrafluoro-1,4-benzoquinone (2a). Phenyldiazomethane (**1**) (0.40 g, 3.4 mmol) in 1,2-di-chloroethane (5 ml) was added over 5 min to a stirred solution of **2a** (0.31 g, 1.7 mmol) in 1,2-dichloroethane (10 ml) at 20 °C. After 1 h stirring, the reaction solution was diluted with benzene up to 50 ml. A two-milliliter aliquot was mixed with a given volume of standard solution of naphthalene in benzene and immediately analyzed by HPLC to determine the absolute yields and isomer ratios of stilbenes (**3**) and spirooxetanes (**4a**). The rest of reaction mixture was concentrated in vacuo and chromatographed on silica gel. Elution with a hexane-benzene mixture (9 : 1, v/v) gave **3** (105 mg, cis/trans=3.5) and increasing benzene (ca. 30% by volume) provided, successively, benzaldehyde (trace), benzaldehyde azine (10 mg), recovered **2a** (72 mg), *trans*-**4a** (74 mg), and *cis*-**4a** (79 mg). The lower cis/trans ratio of isolated **3** may be due to the loss of especially volatile cis-isomer upon evaporation.

Reaction with Tetrabromo-1,4-benzoquinone (2c) and Tetraiodo-1,4-benzoquinone (2d). To a stirred suspension of **2c** (0.72 g, 1.7 mmol) or **2d** (1.05 g, 1.7 mmol) in 1,2-dichloroethane (10 ml) was added a solution of **1** (0.40 g, 3.4 mmol) over 5 min at 20 °C. After 2 h (for **2c**) and 5 h (for **2d**) stirring, the solvent was evaporated. The NMR spectrum of the reaction mixture for **2c** showed the characteristic two doublets (δ=4.88 and 6.88, J=9.0 Hz in CDCl$_3$) assignable to *trans*-**4c**, whereas no such signals were observed for the product mixture for **2d**. The pasty residues were washed with benzene (3×10 ml) to leave recovered quinone **2c** (0.36 g) or **2d** (0.64 g). The washing solutions were diluted with benzene up to 50 ml and a two-milliliter aliquot was used for HPLC analysis as above. Chromatographic treatment of the rest of the reaction mixture of **2c** gave **3** (125 mg, cis/trans=1.1) with a hexane-benzene mixture (9 : 1, v/v), **2c** (0.14 g), benzaldehyde (trace) and benzaldehyde azine (15 mg) with 30% volume benzene in hexane and unidentified resinous products (0.18 g) with a mixture of benzene and ether (20 : 1, v/v). Compound *trans*-**4c** was not obtained in this work-up probably because of decomposition to *trans*-**3** and **2c** on silica gel. Therefore, authentic *trans*-**4c** was prepared by photoaddition of *cis*-**3** (125 mg) and **2c** (300 mg) in benzene (see Table 2). The solvent was evaporated and the residue was dissolved in CDCl$_3$ containing a known amount of 1,1,1,2-tetrachloroethane as internal standard. Analysis of the reaction mixture by NMR spectroscopy showed that the yield of *trans*-**4c** was 54%. Compound **4c** (145 mg, 34%) was carefully isolated by quick chromatography on silica gel with a hexane-benzene mixture (1 : 1, v/v).

Similar column chromatographic separation of the reaction product of **2d** provided **3** (109 mg, cis/trans=1.3), **2d** (0.21 g), benzaldehyde(trace), benzaldehyde azine (34 mg). Later resinous fractions (0.19 g), eluted by increasing benzene and by adding small amount of ether, showed ill-defined peaks in the NMR spectra and could not be identified.

Physical Properties of Diphenylspiro[2,5-cyclohexadiene-1,2′-oxetan]-4-one Derivatives. (The physical properties of *trans*-**4b** are given in elsewhere[6b]).

2,3,5,6-Tetrafluoro-*cis*-3′,4′-diphenylspiro[2,5-cyclohexadiene-1,2′-oxetan]-4-one (*cis*-4a): Colorless prisms (from hexane-benzene); mp 137—138 °C; IR (KBr) 1681, 1305, 993, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.32 (d, J=9.7 Hz, 1H, methine), 6.50 (d, J=9.7 Hz, 1H, methine), 6.6—7.5 (m, 10H, aromatic); UV (THF) $\lambda_{\max}$ 223.5 nm (log ε 4.21), 276 (3.80); MS m/z 254 (M$^+$—PhCHO). Calcd for $C_{20}H_{12}O_2F_4$: C, 66.67; H, 3.36%. Found: C, 66.85; H, 3.41%.

2,3,5,6-Tetrafluoro-*trans*-3′,4′-diphenylspiro[2,5-cyclohexadiene-1,2′-oxetan]-4-one (*trans*-4a): Colorless prisms (from hexane-benzene); mp 124—125 °C; IR (KBr) 1691, 1302, 985, 934, 756, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.03 (d, J=9.0 Hz, 1H, methine), 6.43 (d, J=9.0 Hz, 1H, methine), 7.1—7.7 (m, 10H, aromatic); UV (THF) $\lambda_{\max}$ 219 (log ε 4.17), 231.5 (4.14), λ_{shoul} 270 nm (3.89); MS m/z 254 (M$^+$—PhCHO). Calcd for $C_{20}H_{12}O_2F_4$: C, 66.67; H, 3.36%. Found: C, 66.92; H, 3.36%.

2,3,5,6-Tetrabromo-*trans*-3′,4′-diphenylspiro[2,5-cyclohexadiene-1,2′-oxetan]-4-one (*trans*-4c): Colorless prisms (from hexane-benzene); mp 130 °C (decomp); IR (KBr) 1673, 1561, 1058, 965, 749, 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=4.88 (d, J=9.0 Hz, 1H, methine), 6.88 (d, J=9.0 Hz, 1H, methine), 7.0—7.7 (m, 10H, aromatic); UV (THF) $\lambda_{\max}$ 220 nm (log ε 4.25), 271 (4.00), λ_{shoul} 300 (3.86); MS m/z 423 (M$^+$—PhCH=CHPh). Calcd for $C_{20}H_{12}O_2Br_4$: C, 39.77; H, 2.00%. Found: C, 39.90; H, 2.18%.

Photochemical (2+2) Addition of *cis*- and *trans*-Stilbene (3) with Quinones, 2a, 2c, and 2d. General procedures are exemplified in case of ***cis*-3** and quinone **2a** as follows. Equimolar solution of *cis*-**3** (145 mg, 80 mmol) and **2a** (145 mg, 80 mmol) in benzene (10 ml) was irradiated through Pyrex under nitrogen atmosphere by using a 100 W high-pressure mercury lamp at 20 °C for 4 h. The yields and isomer ratios of photoadducts were determined by means of HPLC or NMR as above.

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