Reactions of Aryldiazomethanes with Chloranil

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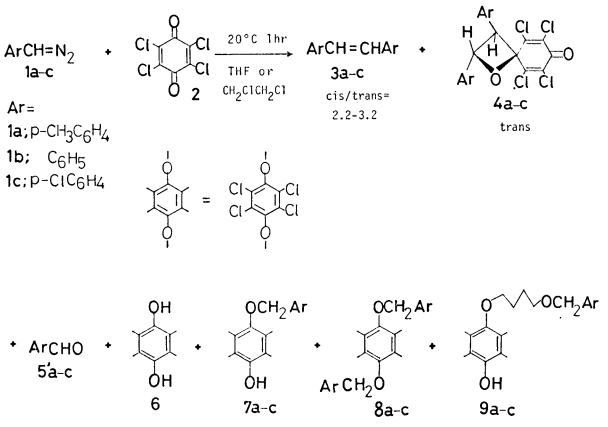
The reactions of several aryldiazomethanes (**1a**: *p*-tolyl; **1b**: phenyl; **1c**: *p*-chlorophenyl) with chloranil gave stilbenes (**3**) and spiro-oxetanes (**4**) at 20 °C in tetrahydrofuran or 1,2-dichloroethane. The isomer ratios of **3** were *ca.* 2 to 3:1 in favor of *cis*, depending on the solvents and on the substituents of **1**. In the case of **4**, however, stable *trans*-isomers were selectively formed. On the other hand, the presence of added CH_3OH suppressed the formations of **3** and **4** and, instead, induced redox reactions giving α,α-dimethoxyarylmethanes and tetrachlorohydroquinone (**6**). In these redox reactions, the acid decompositions of **1** with **6** were also found. However, the presence of CF_3CH_2OH allowed the formation of considerable amount of **3** and **4**, along with the redox products. The mechanism of these reactions will be discussed.

Diazoalkanes are useful synthetic intermediates in organic chemistry and are best represented as resonance hybrid structures with opposing dipoles.[1] These compounds, therefore, behave as 1,3-dipoles[2] or as nucleophiles[3] because of the high electron density on diazo carbon. On the other hand, quinones have conjugated two C=O and two C=C double bonds to be considered as dipolarophiles.[4] Moreover, halogen and/or cyano substituted quinones, such as chloranil and dichlorodicyano-*p*-benzoquinone, become strong electron acceptors.[5] Therefore, the reactions of diazoalkanes with quinones are interesting from the viewpoint of mechanistic study or synthetic application. For example, Pechmann[6] has reported the formation of a pyrazoline derivative through the 1,3-dipolar cycloaddition of diazomethane to the C=C bond of *p*-benzoquinone. In the case of tetrahalo-substituted quinones, epoxides were isolated in the reactions with diazomethane because the C=O bond is more reactive than the C=C bond in these quinones.[7] In this paper, we want to describe the reactions of some aryldiazomethanes(**1**) with chloranil(**2**) with or without added CH_3OH or CF_3CH_2OH.[8]

Results and Discussion

*The Reactions of Aryldiazomethanes (**1a**—**c**) with Chloranil (**2**) in THF or CH_2ClCH_2Cl.* The reactions of **1a**—**c** with **2** gave mainly *cis*- and *trans*-stilbenes(**3a**—**c**) and *trans*-spiro-oxetanes(**4a**—**c**), as is shown in Scheme 1. Besides **3** and **4**, small amounts of several products were isolated: benzaldehydes(**5′ a**—**c**), tetrachlorohydroquinone(**6**), tetrachloro-4-(benzyloxy)phenols(**7a**—**c**), tetrachloro-1,4-bis(benzyloxy)benzenes(**8a**—**c**), and tetrachloro-4-[4′-(benzyloxy)butoxy]phenols (**9a**—**c**). The **9** products were obtained only in the THF solution because these compounds incorporated the THF molecule. Since these by-products were afforded by the action of the residual water present in the solvent, a detailed mechanism will be presented later for the case of the reactions in the presence of CH_3OH or CF_3CH_2OH. The reaction conditions and the product distributions are summarized in Table 1.

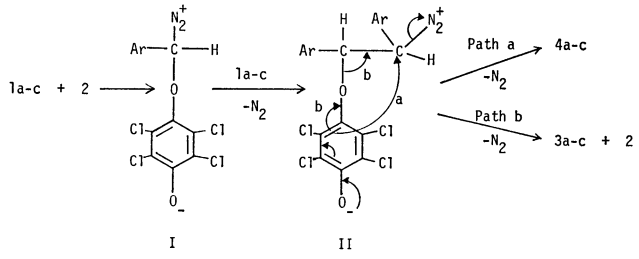


Scheme 1.

In both THF and 1,2-dichloroethane, **3** were major products. The yield of **4** was considerably greater in 1,2-dichloroethane than in THF. Here, particular attention should be paid to the stereochemistry of **3** because the thermodynamically less stable *cis*-isomers were about 2 to 3 times more numerous than the *trans*-isomers, depending on the solvents and on the substituents of **1**. On the other hand, **4** were shown to be the only stable *trans*-isomers by comparison with an authentic sample produced by the photoaddition of *trans*-**3b** and **2**, and also by the fact that the thermal decomposition of **4** at slightly over their melting points for several minutes gave *trans*-**3** and **2**. As is exemplified in the case of **1b** in THF, the ratio of **1** to **2** had no essential influence on the product distributions.

Mechanistically, the formation of **4** needs an intermediate because *cis*- or *trans*-**3** was quantitatively recovered after 5-hs' mixing with an equimolar amount of **2** in THF or 1,2-dichloroethane at room temperature. The most reasonable process is the occurrence of the diazonium betaine intermediate(II) which can produce **4** or **3** by way of Path(a) or Path(b), as is shown in Scheme 2.

Though II may be formed through the nucleophilic attack of **1** on the first diazonium betaine(I, or carbonium betaine given by the loss of N_2), the mechanism



Scheme 2.

Table 1. Product distributions in the reactions of aryldiazomethanes (**1a—c**) with chloranil (**2**) in THF or CH_2ClCH_2Cl at 20 °C[a]

1a—c and **2** (mmol)		Solv.	Yield/%[b]						
			3(*cis*/*trans*)	**4**	**5′**	**6**	**7**	**8**	**9**
1a (7.35)	**2** (2.03)	THF	69.0 (2.4)	15.6	6	2	4	0.5	0.5
1b (8.47)	**2** (2.03)		75.5 (2.8)	8.1	6	1	2.5	0.5	2.5
1b (8.47)	**2** (4.06)		73.7 (2.8)	7.5	7	1.5	2.5	0.5	3
1c (6.58)	**2** (2.03)		72.3 (3.2)	6.2	10	1	4	1	3
1a (7.35)	**2** (3.25)	CH_2Cl | CH_2Cl	60.0 (2.2)	31.7	4	0.5	2	1	—
1b (8.31)	**2** (2.03)		59.7 (2.5)	26.4	6	2	3.5	1	—
1c (5.92)	**2** (2.03)		59.5 (2.9)	20.6	11	3	5	2	—

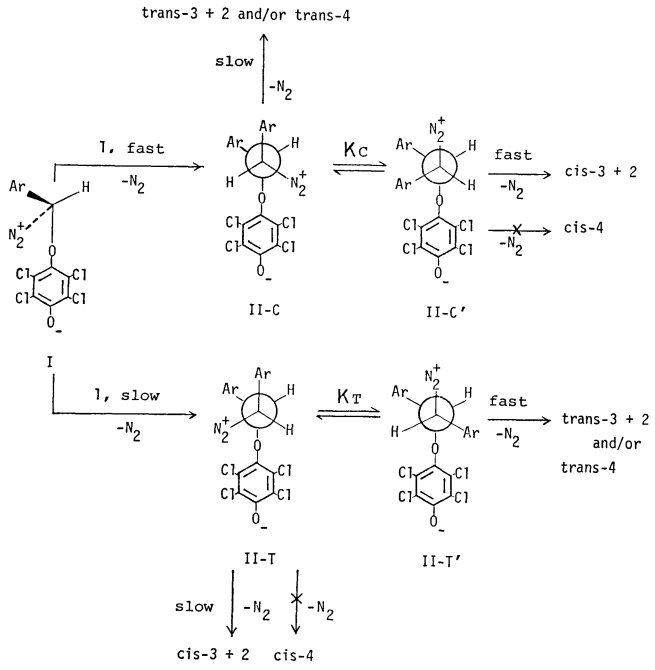
a) Reaction time 1 h. b) Yield as mole percentage based on **1**.

giving I remains unknown. However, three possible routes can be suggested. The first one is the radical-ion formation, followed by the simultaneous recombination presumed in our previous communication.[9] Radical cations of diazoalkanes have already been postulated or actually detected in the electrochemical oxidation[10] or in the reaction with copper(II) perchlorate.[11] However, no direct evidence for the presence of the radical cation of **1** could be obtained in our system, though the radical anion of **2** was detected in the measurements of ESR and electronic absorption spectra.[9] The second possible route is the formation of 2,5-dihydro-1,3,4-oxadiazole through 1,3-dipolar cycloaddition between **1** and **2**; the follow-up ring opening or the loss of N_2 gives I or carbonium betaine. In fact, 1,3,4-oxadiazole was isolated in the reaction of diazomethane with duroquinone.[12] Other examples of the favoring of the 1,3,4-structure of oxadiazole were found in the reactions of diphenyldiazomethane with diphenylketene[13] and of aryldiazomethanes with hexa- and pentafluoroacetones.[14] The last possible route is the direct attack of the diazo carbon on the oxygen atom of **2**. Whichever route is adopted, it has to explain the observation that the qualitaitve N_2 evolution or disappearance of diazo-color was accelerated in the order of **1c**<**1b**<**1a**.

Stereochemistry in the Formations of ***3*** *and* ***4***. The high *cis*-to-*trans* ratio of stilbenes in the decomposition of **1a—c** with catalytic ammonium cerium(IV) nitrate has already reported by Trahanovsky and his coworkers.[15] However, an unequivocal explanation of the high yield of the *cis*-isomer is lacking.

Why does the major path(b) preferentially yield *cis*-isomers rather than *trans*-ones, while the minor path(a) selectively yields *trans*-isomers? These stereochemical phenomena can be well interpreted by considering the transition state leading to II and the subsequent N_2 elimination process giving **3** and **4**. The nucleophilic attack of **1** on I should occur favorably through the transition state where the steric repulsion is as small as possible and where the opposite charges which appear attract each other.

As is pictured in Scheme 3, I contains a large chloranil moiety with a negative charge, a medium-sized aryl group, and a small H atom on the side remote from the N_2^+ group. Therefore, the approach of **1** to I from this side predominantly give such stable conformers as II-C



Scheme 3.

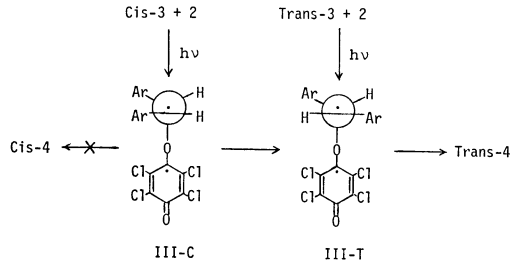
and II-T, avoiding the most striking steric repulsion between the chloranil moiety and the aryl group of **1**, and also satisfying the electronic requirement mentioned above. It should be noted here that the II-C has a lower free energy than II-T because the former can release some of the steric repulsion by placing the small H atom on the most hindered space between the chloranil moiety and the aryl group. Accordingly, the formation of II-C is more accelerated than II-T. However, in the conformational rotation to II-C′ and II-T′, the equilibrium constant, K_C, is apparently smaller than K_T because II-C′ has the highest free energy amoung these four isomers from the sterical point of view(Scheme 3). In view of the steric orientations of these isomers, it may be thought that the stereochemistry of the produtcs depends on how great extent the respective isomers contribute to the product formations. As is represented in Scheme 3, II-C and II-T may produce *trans*-**3** and *cis*-**3** respectively *via* a cis-type elimination; also, II-C may produce *trans*-**4** *via* an intramolecular S_Ni-type reaction. On the other hand, II-C′ and II-T′ may produce *cis*-**3** and

Table 2. Product distributions in the reactions of **1a—c** with **2** in $THF-CH_3OH$ or $THF-CF_3CH_2OH$ and in the reaction of **1b** with **6** in THF at 20 °C[a)]

1a—c, **2**, and **6** (mmol)		Additive[b)]	Yield/%[c)]						
			3(*cis*/*trans*)	**4**	**5′**	**6**	**7**	**8**	**9**
1a (7.35)	**2** (6.10)	CH_3OH	trace	ND[d)]	53	23	22	2	7
1b (8.47)	**2** (8.50)	CH_3OH	trace	ND	52	13	19	3	18
1c (6.58)	**2** (6.10)	CH_3OH	trace	ND	46	12	15	2	17
1b (8.47)	**2** (8.50)	CF_3CH_2OH	58 (2.6)	6	24	11	3.5	1	3.5
1b (8.47)	**6** (8.47)	—	—	—	—	—	43	7	47

a) Reaction time 1 h. b) A four-fold excess was added with respect to **1**. c) Yield as mole percentage based on **1**. d) Not detected.

trans-**3** respectively *via* a trans elimination; also, II-T′ may produce *trans*-**4** *via* an intramolecular S_N2-type displacement. However, II-C′ or II-T can not give *cis*-**4**, probably because of the highly crowded model, which has the two aryl groups on the same side. In accordance with this idea, we obtained *trans*-**4b** alone in a 77.8 or 79.2% yield on the 3-h irradiation of a benzene solution of *trans*- or *cis*-stilbene containing an equimolar amount of **2**(50 mmol dm^{-3}), using a high-pressure mercury lamp at 20 °C: photochemical oxetane formation from olefins and C=O compounds is well known to proceed *via* a biradical intermediate,[16] such as III-C(from *cis*-stilbene) and III-T(from *trans*-stilbene); the former seems to afford no *cis*-**4** because of the highly crowded orientation as well as II-T and II-C′, but it does afford *trans*-**4** after pre-transformation into the stable III-T(Scheme 4).

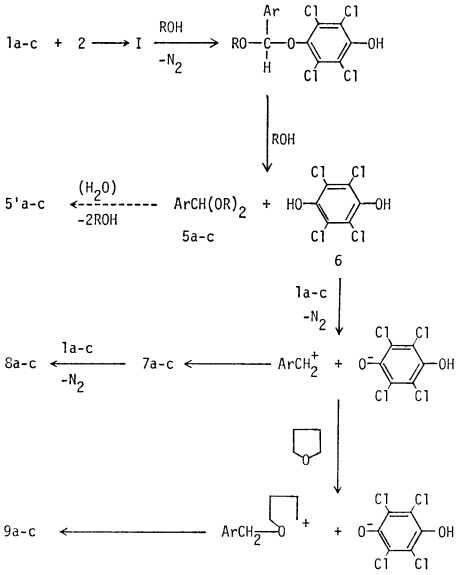


Scheme 4.

From these stereochemical considerations, the present high yield of *cis*-**3** can be reasonably explained as being responsible for the significant contribution of II-C′. Otherwise, the product distributions from the other conformers, II-C, II-T, and II-T′, would result in an excess formation of *trans*-**3** relative to *cis*-**3**, conflicting with the present results (Table 1). Therefore, it may be suggested that the rate of the product formation from II-C′ and II-T′ is much more rapid than that from II-C and II-T.

A further examination of Table 1 indicates the presence of the solvent and the substituent effects on the product distributions. The significant increase in *trans*-**4** in 1,2-dichloroethane compared with the amount in THF may be attributable to the lower solvating ability of the former medium, where the opposite charges of II should come close together, thus retarding the conformational rotation. This phenomenon results in the increase in path(a) and also in the increase of the product formation from II-C and II-T, giving more *trans*-**3** and *trans*-**4**. On the other hand, the substituents of **1** affect the relative ratio of II-C to II-T, since the stronger the nucleophilicity of **1**, the weaker the stereoselective attack of **1** on I becomes, as is supposed by the reactivity selectivity principle.[17] This assumption is in good agreement with the facts that the *cis*/*trans* ratio of **3** decreases, while *trans*-**4** increases, with the increase in the nucleophilic activity of **1**.

Reactions of ***1a—c*** *with* ***2*** *in THF–CH_3OH or THF–CF_3CH_2OH.* To establish the validity of the I intermediate, it is useful to attempt capturing it with suitable nucleophilic reagents. Indeed, marked changes in the product distributions were found on the addition of CH_3OH or CF_3CH_2OH, as is summarized in Table 2. The reactions in the presence of CH_3OH gave only a trace amount of **3**; instead, they afforded mainly acetals(**5**) and **6**, along with **7**, **8**, and **9**. **5** were isolated as benzaldehydes(**5′**) because of the easy degradation under the present acidic conditions as exhibited in the NMR measurement (see Experimental). These phenomena indicate that I undergoes a nucleophilic attack by CH_3OH rather than by **1** to turn into the redox products, as is formulated in Scheme 5. Furthermore, in this Scheme the forma-



Scheme 5.

tion of **6** may be responsible for the products, **7**, **8**, and **9**, because this hydroquinone is so acidic as to decompose **1**, as was confirmed in a comparative experiment using **1b** and **6** (Table 2). Both **7** and **8** are simple mono- and dietherification products of **6** with **1**; however, **9** noticiably arises from the THF ring opening caused by the attack of the resulting benzyl cations.

On the contrary, the presence of CF_3CH_2OH allowed the substantial formation of **3b** and **4b** because of the lesser nucleophilic ability of this alcohol compared with CH_3OH. Keeping these results in mind, the appearance of small amounts of **5'**, **6**, **7**, **8**, and **9** in the absence of an additive may be attributed to the action of the residual water (ROH, R=H) present in the solvent in spite of careful drying; here unstable *gem*-diols seem to be produced instead of **5**.

In summary, aryldiazomethanes behave differently toward chloranil than in the epoxide formation in the case of diazomethane.[7] Stilbenes and spirooxetanes were formed from the intermediate, I, under the stereocontrolled conditions which furnished *cis*-rich for **3** and only the *trans*-isomer for **4**. However, the introduction of CH_3OH markedly changed these reaction features to the redox ones giving acetals and hydroquinone.

Experimental

The NMR spectra were obtained with a Varian EM-360 instrument. The IR and UV spectra were recorded with a Hitachi 215 infrared spectrometer and a 323 spectrophotometer respectively. The ESR spectra were observed with a JEOL JES-NE2X instrument.

Materials. The tetrahydrofuran(THF) was refluxed over lithium aluminum hydride and fractionated. The dichloroethane was dried over anhydrous calcium chloride for several days and fractionated. The methanol was treated with magnesium and fractionated. The 2,2,2-trifluoroethanol(Wako Pure Chemical Co., Ltd. >99%) was used without further purification. The chloranil was commercially obtained and was purified by recrystallization from dry THF; mp 290 °C. The oily aryldiazomethanes (**1a**—**c**) were prepared just before use by the method of Closs and Moss[18] and were used without further purification. Hence, small amounts of benzaldehyde azines given by the spontaneous decomposition of the diazo compounds were detected in the NMR purity check in the cases of **1a** and **1b**; therefore, these azines were discarded in calculating the reaction yields. The NMR signals of the aliphatic protons of these diazo compounds and the corresponding azines (in parentheses) are as follows: δ ($CDCl_3$) **1a**; 4.88 (8.26), **1b**; 4.90 (8.67), **1c**; 4.87.

*Reactions of Aryldiazomethanes (**1a**—**c**) with Chloranil (**2**).* These reactions were carried out in THF and 1,2-dichloroethane. The general procedures are exemplified in the case of **1a** in THF as follows. To a stirred solution of **2** (0.5 g, 2.03 mmol) in 20 ml of dry THF, we added, drop by drop, a THF solution (10 ml) containing **1a** (0.97 g, 7.35 mmol) over a 10-min period at 20 °C. The color of the solution was suddenly darkened by the addition of **1a**, and then it gradually faded with the vigorous evolution of N_2. After 1 h's standing, the removal of the solvent *in vacuo* gave a pasty reaction mixture. The washing of this mixture with 3×20 ml pentane and then with a small portion of ether left recovered **2** (130 mg) and **4a** (260 mg, 15.6%); the amount of **4a** was determined by the NMR measurement using an internal standard ($CHCl_2CHCl_2$, δ=5.8 (s)), while its analytical sample was obtained by fractional crystallization from benzene–petroleum ether. The evaporation of the solvent (pentane–ether) gave an oily residue (1.21 g), which was submitted to NMR measurement. The spectrum showed the formation of excess *cis*-**3a** compared with its *trans*-isomer, as was confirmed by subsequent chromatographic treatment (silica gel). Elution with pentane gave, successively, *cis*-**3a** (374 mg, 49%) and *trans*-**3a** (155 mg, 20%), while elution with a petroleum ether–benzene mixture gave **8a** (8 mg, 0.5%), **2** (55 mg), **5'a** (53 mg, 6%), **7a** (103 mg, 4%), and **9a** (16 mg, 0.5%), and subsequent elution with a benzene–ether mixture gave **6** (40 mg, 2%) and a small amount of an unidentified solid. The structures of **3a**—**c**, **4a**—**c**, **7a**—**c**, **8a**—**c**, and **9a**—**c** were determined by elemental analyses, and the IR and NMR spectra.

p,p'-Dimethylstilbene(*cis*-**3a**); colorless oil. NMR (δ, $CDCl_3$): 2.28 (6H, s, CH_3), 6.45 (2H, s, vinyl H), 6.88—7.20 (8H, q, aromatic H). Found: C, 92.13; H, 7.82%. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74%.

p,p'-Dimethylstilbene(*trans*-**3a**); colorless leaflets (ether); mp 179—180 °C. NMR (δ, $CDCl_3$): 2.30 (6H, s, CH_3), 6.90 (2H, s, vinyl H), 6.95—7.40 (8H, q, aromatic H). Found: C, 92.24; H, 7.80%. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74%.

Stilbene (*cis*-**3b**); colorless oil. NMR (δ, $CDCl_3$): 6.57 (2H, s, vinyl H), 7.22 (10H, s, aromatic H). Found: C, 92.94; H, 6.69%. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71%.

Stilbene(*trans*-**3b**); colorless leaflets (ether); mp 123—124 °C. NMR (δ, $CDCl_3$): 7.07 (2H, s, vinyl H), 7.17—7.57 (10H, m, aromatic H). Found: C, 93.20; H, 6.70%. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71%.

p,p'-Dichlorostilbene(*cis*-**3c**); colorless oil. NMR (δ, $CDCl_3$): 6.47 (2H, s, vinyl H), 7.07 (8H, s, aromatic H). Found: C, 67.38; H, 4.06%. Calcd for $C_{14}H_{10}Cl_2$: C, 67.50; H, 4.02%.

p,p'-Dichlorostilbene(*trans*-**3c**); colorless leaflets (ether); mp 178—181 °C. NMR (δ, $CDCl_3$): 7.0 (2H, s, vinyl H), 7.37 (8H, s, aromatic H). Found: C, 67.09; H, 4.11%. Calcd for $C_{14}H_{10}Cl_2$: C, 67.50; H, 4.02%.

*2,3,5,6-Tetrachloro-*trans-*3',4'-di-*p-*tolylspiro[2,5-cyclohexadiene-1,2'-oxetan]-4-one (**4a**).* Colorless prisms (benzene–petroleum ether); mp 154 °C (dec). IR (KBr): 1675, 1111, 953, 800, 718 cm^{-1}. NMR (δ, $CDCl_3$): 2.35 (3H, s, CH_3), 2.40 (3H, s, CH_3), 4.93 (1H, d, J=9.3 Hz), 6.67 (1H, d, J=9.3 Hz), 6.83—7.60 (8H, m, aromatic H). UV: λ_{max} (THF) 260, 306.5 nm (ε=12900, 6270). Found: C, 58.48; H, 3.56%. Calcd for $C_{22}H_{16}Cl_4O_2$: C, 58.18; H, 3.55%.

*2,3,5,6-Tetrachloro-*trans*-3',4'-diphenylspiro[2,5-cyclohexadiene-1,2'-oxetan]-4-one (**4b**).* Colorless prisms (benzene–petroleum ether); mp 150 °C (dec). IR (KBr): 1671, 1092, 955, 762 cm^{-1}. NMR (δ, $CDCl_3$): 4.98 (1H, d, J=9.1 Hz), 6.72 (1H, d, J=9.1 Hz), 6.90—7.83 (10H, m, aromatic H). UV: λ_{max} (THF) 259, 295 nm (ε=11400, 6995). Found: C, 56.62; H, 2.91%. Calcd for $C_{20}H_{12}Cl_4O_2$: C, 56.37; H, 2.84%.

*2,3,5,6-Tetrachloro-*trans*-3',4'-bis(*p*-chlorophenyl)spiro[2,5-cyclohexadiene-1,2'-oxetan]-4-one (**4c**).* Colorless prisms (benzene–petroleum ether); mp 172 °C (dec). IR (KBr): 1676, 1100, 952, 821, 726 cm^{-1}. NMR (δ, $CDCl_3$): 4.87 (1H, d, J=8.9 Hz), 6.60 (1H, d, J=8.9 Hz), 6.83—7.50 (8H, m, aromatic H). UV: λ_{max} (THF) 260.5, 296 nm (ε=13600, 7320). Found: C, 48.74; H, 2.13%. Calcd for $C_{20}H_{10}Cl_6O_2$: C, 48.52; H, 2.04%.

*2,3,5,6-Tetrachloro-4-(*p*-methylbenzyloxy)phenol (**7a**).* Colorless needles (benzene–petroleum ether); mp 134—135

°C. IR (KBr): 3390, 1437, 1391, 958, 708 cm^{-1}. NMR (δ, $CDCl_3$): 2.35 (3H, s), 4.92 (2H, s), 5.83 (1H, s, OH), 7.05—7.50 (4H, q, aromatic H). Found: C, 47.81; H, 2.88%. Calcd for $C_{14}H_{10}Cl_4O_2$: C, 47.76; H, 2.86%.

*2,3,5,6-Tetrachloro-4-(benzyloxy)phenol (**7b**).* Colorless prisms (benzene–petroleum ether); mp 142—143.5 °C. IR (KBr): 3390, 1436, 1386, 945, 708 cm^{-1}. NMR (δ, $CDCl_3$): 4.92 (2H, s), 5.85 (1H, s, OH), 7.13—7.50 (5H, m, aromatic H). Found: C, 46.09; H, 2.44%. Calcd for $C_{13}H_8Cl_4O_2$: C, 46.14; H, 2.37%.

*2,3,5,6-Tetrachloro-4-(p-chlorobenzyloxy)phenol (**7c**).* Colorless needles (benzene); mp 174—175 °C. IR (KBr): 3400, 1344, 1152, 1082, 808 cm^{-1}. NMR (δ, $CDCl_3$): 4.93 (2H, s), 5.95 (1H, s, OH), 7.40 (4H, s, aromatic H). Found: C, 41.88; H, 1.97%. Calcd for $C_{13}H_7Cl_5O_2$: C, 41.91; H, 1.89%.

*2,3,5,6-Tetrachloro-1,4-bis(p-methylbenzyloxy)benzene (**8a**).* Colorless needles (benzene); mp 211—212 °C. IR (KBr): 2911, 1424, 1352, 956, 799 cm^{-1}. NMR (δ, $CDCl_3$): 2.38 (6H, s), 5.00 (4H, s), 7.17—7.67 (8H, q, aromatic H). Found: C, 58.06; H, 4.02%. Calcd for $C_{22}H_{18}Cl_4O_2$: C, 57.92; H, 3.98%.

*2,3,5,6-Tetrachloro-1,4-bis(benzyloxy)benzene (**8b**).* Colorless needles (ether); mp 169—171 °C. IR (KBr): 1421, 1358, 959, 752, 694 cm^{-1}. NMR (δ, $CDCl_3$): 4.97 (4H, s) 7.1—7.35 (10H, m, aromatic H). Found: C, 56.04; H, 3.38%. Calcd for $C_{20}H_{14}Cl_4O_2$: C, 56.10; H, 3.30%.

*2,3,5,6-Tetrachloro-1,4-bis(p-chlorobenzyloxy)benzene (**8c**).* Colorless needles (benzene); mp 236—237 °C. IR (KBr): 1418, 1355, 959, 801 cm^{-1}. NMR (δ, $CDCl_3$): 4.96 (4H, s), 7.15 (8H, s, aromatic H). Found: C, 48.63; H, 2.46%. Calcd for $C_{20}H_{12}Cl_6O_2$: C, 48.33; H, 2.43%.

*2,3,5,6-Tetrachloro-4-[4'-(p-methylbenzyloxy)butoxy]phenol (**9a**).* Pale yellow prisms (benzene); mp 86—87 °C. IR (KBr): 3150, 1441, 1381, 1168, 1030, 709 cm^{-1}. NMR (δ, $CDCl_3$): 1.66—2.07 (4H, m, CH_2CH_2), 2.33 (3H, s, CH_3), 3.33—3.73 (2H, m, OCH_2), 3.76—4.17 (2H, m, OCH_2), 4.45 (2H, s, OCH_2Ar), 5.93 (1H, s, OH), 7.13 (4H, s, aromatic H). Found: C, 51.08; H, 4.31%. Calcd for $C_{18}H_{18}Cl_4O_3$: C, 50.97; H, 4.28%.

*2,3,5,6-Tetrachloro-4-[4'-(benzyloxy)butoxy]phenol (**9b**).* Pale yellow prisms (benzene); mp 84—85 °C. IR (KBr): 3240, 1445, 1384, 1171, 1041, 714 cm^{-1}. NMR (δ, $CDCl_3$): 1.70—2.10 (4H, m, CH_2CH_2), 3.40—3.8 (2H, m, OCH_2), 3.80—4.10 (2H, m, OCH_2), 4.43 (2H, s, OCH_2Ar), 5.83 (1H, s, OH), 7.18 (5H, s, aromatic H). Found: C, 49.78; H, 4.03%. Calcd for $C_{17}H_{16}Cl_4O_3$: C, 49.78; H, 3.93%.

*2,3,5,6-Tetrachloro-4-[4'-(p-chlorobenzyloxy)butoxy]phenol (**9c**).* Pale yellow prisms (benzene); mp 77—78 °C. IR (KBr): 3140, 1425, 1371, 1152, 1025, 699 cm^{-1}. NMR (δ, $CDCl_3$): 1.70—2.07 (4H, m, CH_2CH_2), 3.40—3.70 (2H, m, OCH_2), 3.80—4.10 (2H, m, OCH_2), 4.77 (2H, s, OCH_2Ar), 5.90 (1H, s, OH), 7.23 (4H, s, aromatic H). Found: C, 45.99; H, 3.36%. Calcd for $C_{17}H_{15}Cl_5O_3$: C, 45.92; H, 3.40%.

*Reactions of **1a—c** with **2** in THF–CH_3OH.* The reactions were carried out in THF containing CH_3OH. The general procedures may be illustrated by the case of **1a**. To a stirred solution of **2** (1.50 g, 6.10 mmol) in THF (50 ml) containing CH_3OH (1.0 g) we added a THF solution (10 ml) of **1a** (0.97 g, 7.35 mmol) over a 10-min period at 20 °C. After 1 h's standing, the removal of the solvent *in vacuo* gave a pasty reaction mixture. The washing of this mixture with 3×20 ml ether left only the recovered **2** (0.49 g); the subsequent evaporation of the ether solution gave oily products. The NMR spectrum of the oily products showed the presence of α,α-dimethoxy-*p*-tolylmethane (**5a**); (δ, $CDCl_3$), 3.28 (6H, s, OCH_3) and 5.30 (1H, s, $CH(OR)_2$). However, this acetal was easily degradated to *p*-tolualdehyde on work-up. Therefore, the acetal was identified as the aldehyde (**5'a**). The column chromatographic treatment of the oily products gave, successively, **3a** (trace), **8a** (35 mg, 2%), **2** (60 mg), **5'a** (470 mg, 53%), **7a** (565 mg, 22%), **9a** (220 mg, 7%), and **6** (420 mg, 23%).

*Reaction of **1b** with **2** in THF–CF_3CH_2OH.* To a stirred solution of **2** (2.09 g, 8.50 mmol) in THF (50 ml) containing CF_3CH_2OH (3.4 g) we added a THF solution (10 ml) of **1b** (1.0 g, 8.47 mmol) over a 10-min period at 20 °C. After 1 h's standing, the removal of the solvent *in vacuo* gave a pasty reaction mixture. The washing of the reaction mixture with 3×20 ml ether left **2** (1.2 g) and **4b** (110 mg, 6%). The ether was evaporated *in vacuo*, and the residue (1.7 g) was chromatographed. Contrary to the case of CH_3OH, a relatively large amount of **3b** (442 mg, 58%, *cis*/*trans*=2.6) was obtained, together with **5'b** (220 mg, 24%), **6** (230 mg, 11%), **7b** (100 mg, 3.5%), **8b** (20 mg, 1%), and **9b** (120 mg, 3.5%).

*Reaction of **1b** with **6** in THF.* An equimolar mixture of **1b** (1.0 g, 8.47 mmol) and **6** in THF (50 ml) gave **7b** (1.23 g, 43%), **8b** (0.13 g, 7%), and **9b** (1.63 g, 47%).

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