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Polar Effects in the Reactions of a Series of Substituted Diphenyldiazomethanes with Chloranil

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The kinetics and products of the reactions of fifteen meta- and para-substituted diphenyldiazomethanes with chloranil were investigated in tetrahydrofuran. The second-order rate constants, k, increased with the electron-donating ability of the substituents, and the values could be correlated with the Yukawa-Tsuno equation: $\log k/k_0 = -1.67(\sigma^0 + 0.66\,\Delta\bar{\sigma}_R^+) + 0.009$, ($r=0.996$). The ρ value, -1.67, indicates the large development of a positive charge at the diazo carbon in the transition state, while the R value, 0.66, confirms the considerable stabilization of the positive charge by the π-electronic contribution of the para substituents. The products of these reactions were the corresponding 2,3,5,6-tetrachlorohydroquinone poly(benzhydryl)ethers, but these polyethers were easily hydrolyzed into the corresponding benzophenones and tetrachlorohydroquinone(HQ). On the other hand, the initial presence of water or methanol as an additive changed the reaction features to give benzophenone or α,α-dimethoxydiphenylmethane, together with HQ. Reaction mechanisms which account for the results are discussed.

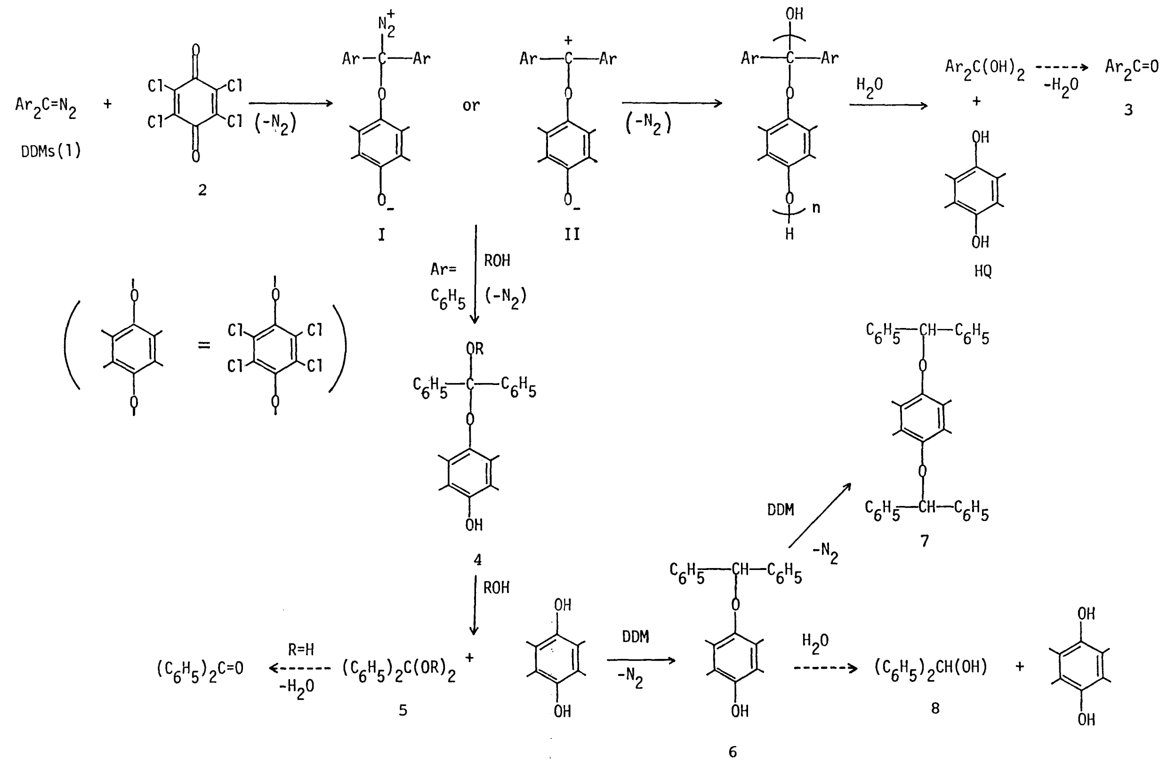
Continuing interest is being paid to the reactions of diazoalkanes with quinones from the synthetic and mechanistic points of view.[1] This is because diazoalkanes are typical 1,3-dipoles[1a,2] with a high electron density on the diazo carbon,[3] while quinones behave as dipolarophiles[1b,4] or electron acceptors[5] with reactive conjugated C=O and C=C bonds. For example, epoxides were obtained when diazomethane was allowed to react with tetrahalo-substituted quinones such as chloranil, because the C=O bonds are more reactive than the C=C bonds in these quinones.[6] We reported in a previous paper[7] that the reactions of several phenyldiazomethanes with chloranil gave stilbenes and spirooxetanes instead of epoxide. We will now extend the diazoalkanes–chloranil systems to a series of diaryldiazomethanes and will describe the kinetics and the mechanism.

Results and Discussion

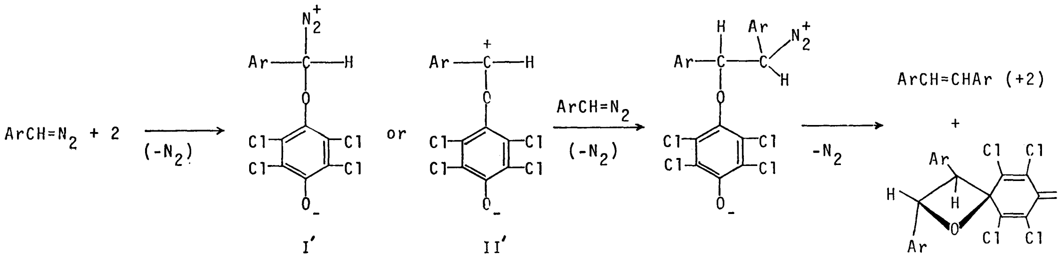
Product Studies. The reactions of diphenyldiazomethane (DDM) and its fourteen meta- and para-substituted analogues (DDMs) (**1**) with an equimolar amount of chloranil (**2**) were conducted in tetrahydrofuran at 30 °C. The decomposition rates were found to be much more accelerated with the increase in the electron-donating abilities of the substituents. For example, the presence of *p,p'*-dimethoxy substituents instantaneously brought about the deposition of a white precipitate, accompanied by a vigorous evolution of N_2, while *p*-nitro-substituted DDM needed one week for the complete disappearance of the diazo color. All these reactions gave some precipitates or suspensions which were easily degradated into the corresponding substituted benzophenones (**3**) and tetrachlorohydroquinone (HQ) on standing in atmospheric moisture or by the addition of aqueous THF. Moreover, the crude reaction mixtures were also completely changed into almost equimolar amounts of the corresponding **3** and HQ on treatment with aqueous THF. These hydrolyses show the stoichiometry to be 1 mol of DDMs to 1 mol of **2**, while the total yields of **3** or HQ are, in most cases, greater than 93%. An elemental analysis of the precipitate obtained in the case of DDM exhibited a composition (C; 54.35, H; 2.46%) very close to the combined molecular formula, $C_{19}H_{10}Cl_4O_2$, of diphenylmethylene and **2**. The IR spectrum (KBr) of this precipitate showed a weak absorption in the OH region, but no appreciable C=O absorption was observed, indicating that the quinonoid structure of **2** has already been lost.

From this chemical and spectroscopic information, it is natural to consider that the structure of these hydrolyzable products is made up by the polyether linkage depicted in Scheme 1. These polyethers consist of an alternate combination of diarylmethylenes and a chloranil moiety with a benzenoid functionality. Accordingly, it can be suggested that intermediary diazonium betaines(I) or carbonium betaines(II) play an important role in the present polymerization process. The propagation of the polyether linkage may be terminated by the action of residual water present in the solvent, the end groups thus becoming hemiketalic OH and phenolic OH. Therefore, the polymerization degree (n) will lie at a lower value with an increase in the water content; we could not estimate the value of n because the precipitates were not soluble in common aprotic solvents and were easily hydrolyzable. The degradation of these polyethers under the influence of water is caused by the successive hydrolytic cleavage of the ether linkage; the dihydroxydiarylmethanes thus formed are easily converted into **3** with a loss of water.

On the other hand, the initial presence of a large amount of water is expected to give, exclusively, the unstable ether (**4**), capable of undergoing subsequent hydrolysis. Indeed, the presence of a five-fold excess of water (ROH, R=H) in the DDM–**2** system brought about the formation of benzophenone and HQ, in addition to small amounts of benzhydrol (**8**) and tetrachlorohydroquinone dibenzhydryl ether (**7**) (Scheme 1). These two by-products seem to be derived from the acid-induced decomposition of DDM with the resulting HQ; the formation of **8** can be ascribed to the hydrolysis of tetrachlorohydroquinone benzhydryl ether (**6**) on work-up. A similar reaction was found in the presence of methanol ($R=CH_3$), where α,α-dimethoxydiphenylmethane (**5**, $R=CH_3$) was



Scheme 1.



Scheme 2.

afforded instead of benzophenone.[8] These solvolysis reactions evidently confirm the occurrence of an intermediate I or II.

Interestingly, the present reactions gave neither olefins nor spirooxetanes; this is in dramatic contrast to the case of phenyldiazomethanes.[7] These products were well explained as arising from the subsequent nucleophilic attack of the diazoalkanes on the diazonium(I′) or carbonium betaine(II′) intermediate, as provided in the present system (Scheme 2). The reason why I or II reject such a nucleophilic attack is probably to be attributed to two factors. One is the steric hindrance due to the presence of two aromatic rings, which screen the central carbon atom from the nucleophilic attack of DDMs. The other is the lesser nucleophilic reactivity of the carbon atom of DDMs compared to that of phenyldiazomethanes. Consequently, the only possible behavior of I and II is to polymerize each other in the absence of strong nucleophiles.

Kinetic Studies. As was noticed in the product studies, the disappearance of the color of the DDMs was much accelerated by introducing the electron-donating substituents in the meta and the para positions of the aromatic rings of DDMs. In order to estimate these polar effects in more detail, the decompositions of fifteen meta- and para-substituted DDMs were followed spectrophotometrically in the presence of high dilute DDMs with respect to **2**; moderate reaction rates were thereby attained, thus avoiding the precipitate formation. The rates determined by monitoring the decrease in the diazo color were found to obey a simple pseudo-first order kinetic law. The rate constants (k_{obsd}) of the decomposition of DDM with various concentrations of **2** are shown in Table 1; the linear dependence of k_{obsd} on the concentration of **2** is held within the limits of experimental error: $10^5 k_{\text{obsd}}/\text{s}^{-1} = 535[\text{Chloranil}]-0.31$. Therefore, the second-order rate constants, k, were obtained simply by dividing the k_{obsd} by the concentration of **2**. The values of k thus determined for the meta- and the para-substituted DDMs at various temperatures are given in Table 2, together with the activation parameters. It can be noted that the *p,p′*-dimethoxy substituents caused a 2500-fold increase in the rate compared with the *p*-nitro substituent at 30 °C. In the case of DDM, the rate of the decomposition was also determined by monitoring the evolved N_2, and the second-order rate constant was nearly equal to that determined by the spectroscopic method. This means that there is no accumulation of any type of intermediate with the N_2 group in the course of the reaction.

The dependence of log k/k_0 on the Hammett σ constants[9] and the Brown σ^+ constants[10] is shown in Fig. 1. For disubstituted DDMs, the σ and the σ^+ values used are the sums of the values for the two substituents. Four meta-substituted DDMs gave an excellent linear dependence ($\rho=-1.52$), $r=0.996$ (correlation coefficient) when the simple Hammett equation and normal σ values were used. When correlating the series of fifteen meta- and para-substituted DDMs and using the normal σ values, though, we obtained substantially worse results ($r=0.933$, $\rho=-2.10$). The correlation line appears to curve upward from the meta line. The replacement of σ by σ^+ caused a considerable improvement in the correlation ($r=0.980$, $\rho=-1.37$), though a downward deviation from the meta line is still found for the methoxy-substituted DDMs. Neither the σ nor σ^+ values apparently fit the correlation of the para-substituted DDMs well.

Therefore, we used the two-parameter Yukawa-Tsuno equation,[11] log $k/k_0=\rho\ (\sigma^0+R\Delta\bar{\sigma}_R^+)$, where σ^0, R, and $\Delta\bar{\sigma}_R^+$ are the normal substituent constant, the resonance reaction constant, and the resonance substituent constant respectively. The results of regression anal-

Table 1. Observed first-order rate constants, k_{obsd}, for the decomposition of DDM(1.70×10^{-3} mol dm^{-3}) with a large excess of chloranil (**2**) in tetrahydrofuran at 40 °C

10^2[Chloranil] mol dm^{-3}	$10^4\ k_{obsd}$ s^{-1}
8.33	4.41
6.66	3.59
5.83	3.01
5.00	2.68
4.16	2.17
3.33	1.76

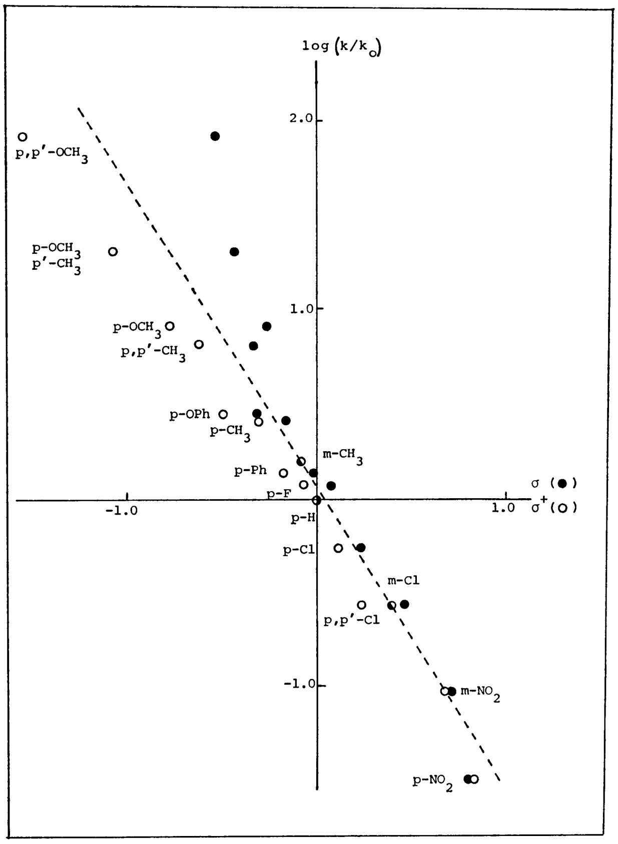


Fig. 1. The plot of log k/k_0 against the Hammett σ(●) and Brown σ^+(○) constants.

Table 2. Second-order rate constants, k, and activation parameters for the decompositions of the substituted DDMs (**1a**—**o**) with chloranil (**2**) in tetrahydrofuran

DDMs	Substituents	$10^3\ k$/l mol^{-1} s^{-1} 30 °C	40 °C	50 °C	ΔH^* kJ/mol	ΔS^* J/mol K
1a	p,p'-OCH$_3$	197	—	—	—	—
1b	p-OCH$_3$, p'-CH$_3$	49.0	—	—	—	—
1c	p-OCH$_3$	19.5	38.9	69.9	49.3	−115
1d	p,p'-CH$_3$	15.8	33.1	62.3	53.2	−104
1e	p-OPh	6.67	13.8	25.7	52.3	−114
1f	p-CH$_3$	6.10	12.0	24.3	53.7	−110
1g	m-CH$_3$	3.71	7.59	14.9	54.0	−113
1h	p-Ph	3.38	6.03	11.2	46.2	−140
1i	p-F	2.80	5.63	11.3	54.2	−115
1j	p-H	2.43 (2.62)[a)]	5.35	10.9	58.5	−102
1k	p-Cl	1.29	2.77	5.31	55.0	−119
1l	p,p'-Cl	0.661	1.41	2.94	58.2	−114
1m	m-Cl	0.623	1.38	2.85	59.3	−111
1n	m-NO$_2$	0.232	—	—	—	—
1o	p-NO$_2$	0.0790	—	—	—	—

a) The value in parentheses was determined at 30.5 °C by the volumetric method employing a 2-molar excess of **2** with respect to DDM.

TABLE 3. SOLVENT DEPENDENCE OF THE RATE CONSTANTS, k, AND THE ACTIVATION PARAMETERS FOR THE DECOMPOSITION OF DDM WITH CHLORANIL (**2**)

Solvent	$DN(-\Delta H_{\mathrm{SbCl_5}})$	E_T	$10^3\,k/\mathrm{l\ mol^{-1}\ s^{-1}}$			ΔH^*	ΔS^*
			30 °C	40 °C	50 °C	kJ/mol	J/mol K
1,2-Dichloroethane	0	41.9	30.5	62.5	111	50.1	−109
Acetonitrile	14.1	46.0	23.4	49.3	85.8	50.2	−110
Ethyl acetate	17.1	38.1	5.34	10.4	20.1	51.2	−119
Benzene	0.1	34.5	2.66	6.09	12.3	59.7	−92.2
Tetrahydrofuran	20.0	37.4	2.43	5.35	10.9	58.5	−102

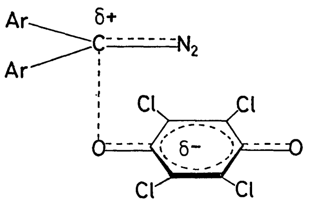
ysis indicate that the use of a two-parameter equation improves the correlation significantly (Eq. 1):

$$\log k/k_0 = -1.67(\sigma^0+0.66\Delta\bar{\sigma}_R^+) + 0.009, \quad (r=0.996,\ s=0.08,\ n=15) \qquad (1)$$

The negative sign and the magnitude of ρ (−1.67) are consistent with the large development of a positive charge at the diazo carbon in the activation process. The value of R=0.66 also confirms that a considerable resonance stabilization of the transition state is required in the present system.

The dependence of the rate on the solvents shows an acceleration or a retardation unexpected from the solvent parameters, *e.g.*, the E_T values (Table 3).[12] A similar unexpected tendency has been observed in the reaction of DDM with tetracyanoethylene (TCNE).[13] These phenomena seem to be ascribable to the stabilization of the initial state caused by the formation of donor–acceptor complexes between these electron acceptors and the solvents. In fact, TCNE is well known to form a strong complex with THF,[14] where the most retarded rate was observed. When the rates were examined as a function of the solvent donor number (DN),[15] the measure of the solvent donability, a decrease in the rate with the increase of DN was always found except in the case of benzene. This exception may be responsible for the lowest E_T value among these solvents, because the charge-separated transition state is not sufficiently solvated in such a nonpolar medium. In this manner, the stabilization of the initial state is so pronounced in the solvent with a high donor number that the rate is no longer directly correlated with the solvent polarities.

Mechanistically, the formation of polyether and the occurrence of the solvolysis reaction in the present system can be well explained by assuming the participation of the diazonium betaine(I) or the carbonium betaine(II) intermediate, as just as in the case of the reactions of phenyldiazomethanes with **2**.[7] The kinetic data presented in this paper provide some information concerning the transition state. The large negative entropies of activation are indicative of the highly ordered transition state usually encountered in 1,3-dipolar cycloaddition.[16] However, the magnitude of the charge separation, as revealed by the Hammett correlation as well as by the solvent effects, appears unmatched in the isopolar transition states of 1,3-dipolar additions. Therefore, the present system is postulated to proceed through the polar transition state depicted below, though the polar transition state of 1,3-dipolar addition[17] can not be ruled out.



Experimental

The IR and NMR spectra were recorded on Hitachi 215 and Varian EM-360 spectrometers respectively. The UV spectra were observed with Hitachi 323 and JASCO UVIDEC 505 instruments.

Materials. The chloranil was of commercial origin and was recrystallized twice from benzene; mp 290 °C. All the diaryldiazomethanes were made by the oxidation of the corresponding hydrazones with yellow mercury(II) oxide as has been previously described.[18] The physical properties of these diazoalkanes were all listed in a previous paper[13] except for *p*,*p*′-dimethoxy-(mp 100—101 °C (ether) (lit,[9] mp 99—100 °C), UV: $\lambda_{\max}$=540 nm (ε=85, THF)), *m*-nitro-(mp 53—54 °C(petroleum ether–ether)(lit,[20] an oil), UV: 500 nm (ε=138, THF)), and *p*-nitrodiphenyldiazomethane (mp 80—82 °C (petroleum ether–ether) (lit,[20] mp 80—83 °C), UV: 500 nm (ε=326, THF)). The THF and benzene were refluxed over lithium aluminum hydride and then fractionated. The acetonitrile and 1,2-dichloroethane were refluxed over phosphorus pentaoxide and then fractionated. The ethyl acetate was dried over anhydrous calcium carbonate and then fractionated.

Kinetic Measurements. In order to satisfy the requirements of pseudo first-order treatment, the kinetic reactions were usually carried out in the presence of a 20- to 50-fold molar excess of **2** with respect to DDMs. The change in optical density at the wavelength of the absorption maxima (524—525 nm) of DDMs (**1a**—**m**) was conveniently monitored because **2** in THF is transparent in this region. The procedure was similar to that described in a previous paper.[13] In the case of the nitro-substituted DDMs (**1n**,**o**), however, the temperature of the reaction solutions was kept at 30±0.1 °C by the use of a Haake circulator, and the absorption at 500 nm was followed over a 70-percent decomposition at certain time intervals. The pseudo first-order rate constants (k_{obsd}) were determined graphically from plots of $-\ln x$ against the time, where x is the concentration of the remaining DDMs. In all cases, excellent straight lines were obtained. Then, the second-order rate constants (k) obtained by dividing k_{obsd} with the initial concentration of **2** were reproducible to within ±3% (usually two determinations).

Reactions of Diaryldiazomethanes (DDMs) with **2** *in THF.* The reaction of diphenyldiazomethane (DDM) will be described below as a typical example; the reactions of the other DDMs were carried out similarly until the characteristic color of the diazo compounds had faded. To a THF solution (40 ml) of **2** (1.0 g, 4.07 mmol) we added, all at once, a THF solution (20 ml) containing DDM (0.79 g, 4.07 mmol) at 30 °C. The purple color of DDM slowly disappeared with a slight evolution of N_2. After 6 h standing, the precipitate (0.8 g) which appeared was filtered, dried *in vacuo*, and submitted to IR measurement and elemental analysis. This white precipitate was completely hydrolyzed to benzophenone and HQ on 3 d exposure to atmosphere or by the addition of aqueous THF. The removal of the solvent, followed by the column chromatography (silica gel) of the hydrolyzed mixtures gave almost equimolar amounts of benzophenone (0.34 g, 46.0%) and HQ (0.47 g, 46.5%), with benzene and ether as the eluents. The filtrate from the white precipitate was dried *in vacuo*, and the residue was treated with a small portion of aqueous THF for 1 h. The column chromatography of the hydrolyzed mixtures also gave equimolar amounts of benzophenone (0.37 g, 50.0%) and HQ (0.52 g, 51.5%). The benzophenones (**3a**—**o**) were identified by a comparison of their IR and NMR spectra with those of authentic samples produced by the Friedel-Crafts reaction. The HQ was identified by a comparison of its IR spectrum with that of an authentic sample.[21]

*Reaction of Diphenyldiazomethane (DDM) with **2** in H_2O–THF.* To a THF solution (40 ml) of **2** (1.0 g, 4.07 mmol) we added, all at once, a THF solution (20 ml) containing DDM (0.79 g, 4.07 mmol) and H_2O (0.36 g, 20 mmol) at 30 °C. After 6 h standing, the removal of the solvent, followed by column chromatography, gave tetrachlorohydroquinone dibenzhydryl ether (**7**) (40 mg, 3.4% based on DDM used), recovered **2** (0.10 g, 10%), and benzophenone (0.64 g, 86%) with a petroleum ether-benzene mixture, and then HQ (0.85 g, 84%) and benzhydrol (**8**) (50 mg, 6.7%) with a benzene–ether mixture. The product, **7**, was recrystallized from benzene; mp 190—192 °C; IR (KBr): 1407, 949, and 689 cm^{-1}; NMR (δ, $CDCl_3$) 6.43 (2H, s) and 7.28 (20H, s); Found: C, 66.05; H, 3.89%. Calcd for $C_{32}H_{22}Cl_4O_2$: C, 66.23; H, 3.82%. Compound **7** was identified by a comparison of its IR and NMR spectra with those of an authentic sample given by the reaction of DDM with HQ.

*Reaction of DDM with **2** in CH_3OH–THF.* The reaction was carried out under conditions similar to those described in the H_2O–THF system. After 6 h standing, the removal of the solvent gave a pasty reaction mixture, the NMR spectrum of which showed the presence of large amounts of α,α-dimethoxydiphenylmethane (**5**). However, the **5** slowly hydrolyzed into benzophenone in the reaction mixture, so that the product analyses were made according to two different procedures. First, one-half of the reaction mixture was washed with 3×20 ml pentane to extract the **5**. The pentane solution was shaken with a small portion of aqueous $NaHCO_3$ (5%), washed with water, and dried over sodium sulfate. The concentration of the filtrated solution yielded crystalline **5** (0.39 g, 85%), mp 106—107 °C; IR (KBr): 1209, 1085, 1053, 987, and 689 cm^{-1}; NMR (δ, $CDCl_3$) 3.10 (6H, s, OCH_3) and 7.13—7.57 (10H, m, aromatic H); Found: C, 78.98; H, 7.01%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%. Second, the other half of the reaction mixture was chromatographed (silica gel). Elution with a petroleum ether–benzene mixture successively afforded **7** (25 mg, 4%), the recovered **2** (0.11 g, 11%), and benzophenone (0.31 g, 84%), while elution with a benzene–ether mixture gave HQ (0.42 g, 83%) and **8** (30 mg, 8%). Thus, **5** was completely hydrolyzed to give benzophenone during the isolation process by the chromatography.

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