The Reaction of Benzil with Grignard Reagents

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Benzil reacts with Grignard reagents forming, in the first step, the 1,2-addition product (*C*-alkylation), but often also the 1,4-addition product (*O*-alkylation) and the reduction product, benzoin. The product distribution has been determined for mechanistic purposes for 16 Grignard reagents using a standard procedure. These results, and observations made using deuteriated reagents and the 5-hexenyl radical probe indicate an electron transfer (ET) mechanism for reagents having hydrogen in the β-position, while a polar mechanism is the most efficient for methyl, phenyl, benzyl and allyl Grignard reagents in ether solution.
For the ET mechanism, a six-centre transition state is suggested. Furthermore, a distinction is made between the primary cage product (*O*-alkyl) resulting from immediate combination of the radical pair, and the secondary cage product (*C*-alkyl) formed in the cage after rearrangement. 5-Hexenylmagnesium bromide yields uncyclised primary and secondary cage product, but also significant amounts of cyclised *C*-alkylation product formed by escape of the radicals from the cage and re-encounter after cyclisation of 5-hexenyl to cyclopentylmethyl.
A recently suggested mechanism based on the existence of stable radical ion pairs is found to be unacceptable.

Reports in the literature on useful applications of the title reaction are limited to Grignard reagents, RMgBr, in which the radical R has no β-hydrogen, such as methyl-, phenyl-, benzyl- and allylmagnesium bromide.[1,2,3] Attempts to use butyl- or cyclohexylmagnesium bromide failed to produce more than trace amounts of identifiable products. The mechanism of the reaction has recently been studied by means of ESR (see below).

In the present work, the reaction of benzil with 16 Grignard reagents has been studied for mechanistic purposes by analysing the product distributions using various solvents and various reaction conditions.

Being a non-enolisable α-diketone, benzil may be attacked once or twice by the Grignard reagent; however, while the first attack was found to be instantaneous, the second attack was usually suficiently slow to allow the two steps to be studied separately.

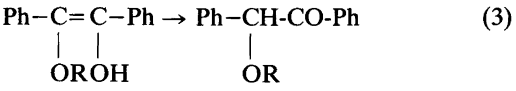
In general, three products were produced in the first step: The normal 1,2-addition product (*C*-alkylation product, CAP), the reduction product (benzoin) and, surprisingly, an *O*-alkylation (OAP) product formed according to eqn. (1).

$$\mathrm{PhCOCOPh + RMgX \rightarrow Ph{-}\underset{\displaystyle \underset{\displaystyle \mathrm{OROMgX}}{|}}{\overset{\displaystyle \overset{\displaystyle \mathrm{H^+}}{\rightarrow}}{\mathrm{C{=}C}}}{|}}{-Ph} \rightarrow \mathrm{Ph{-}\underset{\displaystyle \underset{\displaystyle \mathrm{OROH}}{|}}{\overset{\displaystyle \overset{\displaystyle \mathrm{H^+}}{\rightarrow}}{\mathrm{C{=}C}}}{|}}{-Ph} \qquad (1)$$

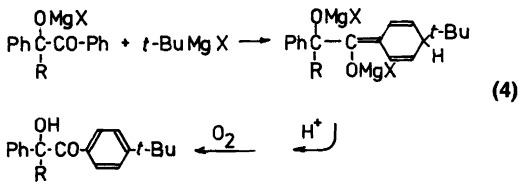
The alkoxy enol produced in this way could be examined by NMR, but the observation required complete absence of oxygen since very rapid oxidation took place in air with the formation of benzoic ester and benzoic acid [eqn. (2)].

$$\mathrm{Ph{-}\underset{\displaystyle \underset{\displaystyle \mathrm{OROH}}{|}}{\mathrm{C{=}C}}{|}{-Ph} + O_2 \rightarrow PhCOOR + PhCOOH} \qquad (2)$$

Rearrangement of the enol took place slowly at room temperature and rapidly at 150 °C, with the formation of a stable alkoxy ketone [eqn. (3)].



(3)

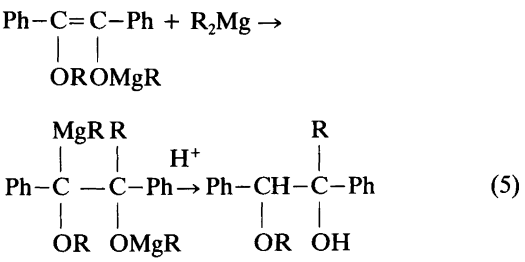


(4)

The relative yields of the three primary reaction products CAP, OAP and benzoin, produced in the reaction of benzil with 16 Grignard reagents in diethyl ether were determined by GLC and HPLC. The reaction was run using a standard procedure designed to include only the products of the first attack on benzil. If secondary products were unavoidable, they were grouped together with the appropriate monoalkylated product. The results are given in Table 1.

Products obtained by two attacks of Grignard reagent included those formed by double *C*-alkylation and *C*-alkylation plus reduction. The use of *t*-butyl reagents produced *C*-alkylation and 1,6-addition to the second carbonyl [eqn. (4)].

The use of the highly reactive, halogen-free dialkylmagnesium led to a combination of *O*-alkylation and *C*-alkylation, presumably according to eqn. (5).



(5)

In experiments with methyl, phenyl, and benzyl

Table 1. Relative product distribution (%), as determined by chromatography, in the reaction of benzil with RMgBr using the standard procedure.

R in RMgBr	CAP			OAP			Benzoin	
	Compound No.	Ether	THF	Compound No.	Ether	THF	Ether	THF
CH_3	**2**	99	99	**3**	0.1		Trace	Trace
CH_3CH_2	**4**	28.2	56	**5**	57.5	34	14.2	10
CD_3CH_2		29.4			58.3		12.3	
$(CH_3)_2CH$	**6**	35		**7**	45		20	
C_4H_9	**8**	30		**9**	56		14	
$(CH_3)CHCH_2$	**10**	47		**11**	30		23	
$(CH_3)_2CDCH_2$		47			32		21	
s-C_4H_9	**12**	30		**13**	40		30	
$(CH_3)_3C-$	**14**	43		**15**	17		40	
$(CD_3)_2(CH_3)C-$		50			19		30	
$CH_2=CH-CH_2$	**16**	99			0		Trace	
$C_6H_5CH_2$	**17**	98			0		2	
C_6H_5	**18**	99	74	**19**	Trace	25	0	Trace
$2-CH_3C_6H_4$	**20**	97		**21**	3			
$4-CH_3C_6H_4$	**22**	99	90	**23**	Trace	10		Trace
$2,4,6-(CH_3)_3C_6H_2$	**24**	80		**25**	20			
$(C_2H_5)_2Mg$		52	67		38	26	10	7
$(C_4H_9)_2Mg$		56			33		11	
$CH_2=CH-(CH_2)_4$	**26**			**27**				
c-$C_5H_9CH_2$	**28**			**29**				

Grignard reagents, small amounts of benzil were found in the reaction mixture. This is probably due to capture of benzil by the magnesium alcoholate formed [eqn. (6)], this reaction being fast

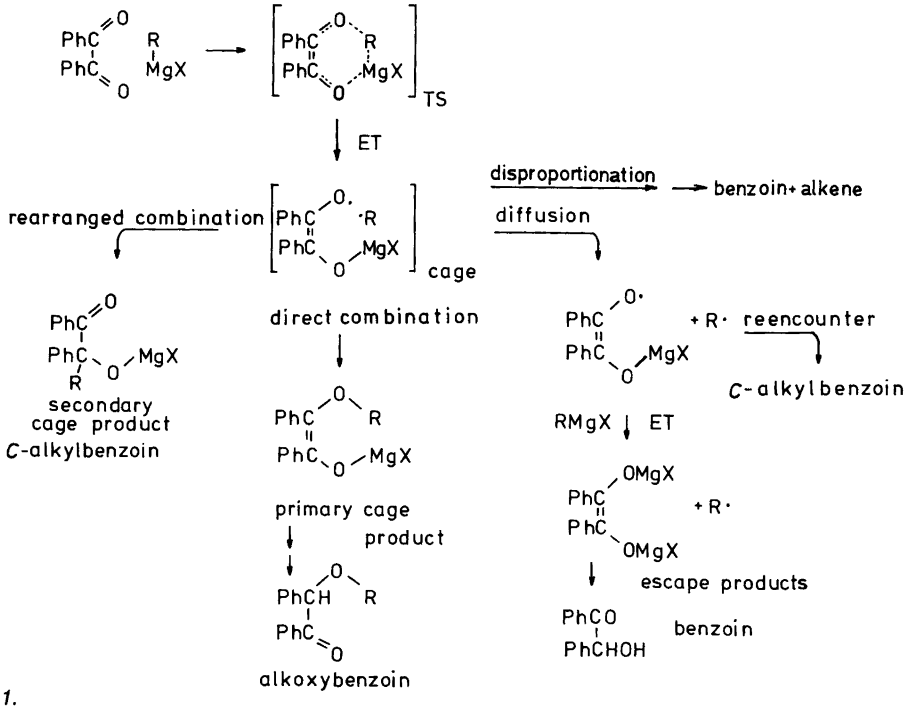
$$\mathrm{PhCOCOPh + ROMgX \rightarrow Ph{-}\overset{\displaystyle OMgX}{\overset{|}{C}}{-}CO{-}Ph} \quad (6)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \overset{|}{OR}$$

enough to compete with the Grignard addition; benzil was subsequently released in the work-up by the addition of acid. This side reaction was found only with phenyl, methyl and benzyl Grignard reagents, and these reagents were therefore considered to be of relatively low reactivity.

Using ether and the standard procedure, no OAP was found in the reaction of the non-reducing methyl, phenyl, allyl, and benzyl Grignard reagents. The use of inverse addition (addition of Grignard reagent to the substrate), however, resulted in the production of small amounts of OAP and benzoin. The choice of solvent was also important, since phenylmagnesium bromide in ether produced only traces of OAP, while a 25 % yield was obtained in THF solvent.

o-Tolyl- and mesitylmagnesium bromide in ether yielded 3 and 20 % *O*-arylated product, respectively, increasing to 20 and 60 % using inverse addition.

O-Alkylation by Grignard reagents is known from reactions with *ortho*-quinones and *ortho*-quinol acetates and is assumed to take place by an electron transfer (ET) mechanism.[4,5,6,7] Benzil is also an obvious candidate for an ET mechanism, since it is a good electron acceptor forming a very stable semidione radical of which one important resonance form has the unpaired spin on oxygen, while another resonance form has the spin on carbon. Scheme 1 shows the ET mechanism, which may account for the production of CAP and OAP as well as benzoin. The transfer of the electron and of magnesium are shown as a single step, but they may be more or less separated. The ketylmagnesium radical and the alkyl radical are formed in the solvent cage and may react in three ways to afford the three reaction products, all by reaction within the cage. If the radicals diffuse out of the cage, the ketyl will ac-



Scheme 1.

cept an electron from an additional molecule of Grignard reagent and form benzoin and an alkyl radical. The radicals will, if they are relatively stable, react with each other; if they are unstable, e.g. phenyl, they may react with the solvent, abstracting a hydrogen atom.

The "escape mechanism" for formation of benzoin is the only one possible if the radical R of the Grignard reagent has no β-hydrogen, like benzyl, whereas benzoin formed in the reaction with ethylmagnesium bromide may be either a cage product (radical disproportionation) or an escape product.

It was possible to choose between these alternatives by using Grignard reagents having deuterium instead of hydrogen in the β-position. In the cage mechanism, deuterium substitution would make combination to benzoin less favourable and diminish the yield, while in the escape mechanism (diffusion), the yield of benzoin would be unchanged. The latter was found to be the case using β,β,β-trideuterioethyl- and β-deuterioisobutylmagnesium bromide (see Table 1). The reduction in the yield of benzoin on deuteriation is only ca. 10 %, and its formation in the reaction therefore involves an electron transfer to the ketyl which has escaped from the cage. In the case of β-deuteriated *t*-butylmagnesium chloride, however, the relative yield of benzoin was lowered significantly, indicating some abstraction of a β-hydrogen from the *t*-butyl radical by the ketyl radical within the cage.

The effect of β-deuteriation on the *O*-alkylation/*C*-alkylation ratio was within the limits of experimental accuracy. This indicates that in the case of ethyl and isobutyl Grignard reagents, there is no competition between an ET and a polar mechanism, since opposite secondary kinetic isotope effects would be expected for the two mechanisms.

For methyl- and phenylmagnesium bromide reacting in ether solution it is doubtful, however, whether the mechanism involves electron transfer, since practically no *O*-arylated product or benzoin is produced. Phenyl and methyl Grignard reagents are poor electron donors and at the same time are very reactive nucleophiles. In the polar reaction with acetone, phenyl- is many times more reactive than ethyl magnesium bromide, while the situation is opposite in the SET reaction with benzophenone.[8] Changing the solvent to THF apparently favours the ET mechanism for phenylmagnesium bromide, as seen by the formation of 25 % of phenoxybenzoin as well as small amounts of benzoin.

Table 2. Relative product distribution (HPLC) of addition products in the reaction of benzil with butylmagnesium bromide containing 7.4 % of isobutylmagnesium bromide using the standard procedure.

Product	%
Benzoin isobutyl ether	2.5
Benzoin butyl ether	65.3
α-Isobutylbenzoin	2.4
α-Butylbenzoin	29.7

Besides favouring the ET over the polar mechanism, THF generally favours the production of CAP. Ether, on the other hand, favours the production of OAP. At −70 °C, ethylmagnesium bromide in ether yields 90 % OAP; the same reaction in THF affords 90 % CAP at −70 °C.

A clue to an explanation was obtained from experiments using the radical probe 5-hexenylmagnesium bromide. This reagent always contains a certain amount of the cyclised cyclopentylmethylmagnesium bromide, in the present case 7.4 %. The reagent was allowed to react with benzil, using the standard procedure and also using equimolar amounts of the reactants. Since product formation in the first type of experiments is dependent, amongst other things, on the competition between the cyclic, β-branched reagent and the straight chain hexenylmagnesium bromide, a model reaction was performed for comparison, using 7.4 % of isobutylmagnesium bromide (β-

Table 3. Relative product distribution (%, HPLC) of addition products in the reaction of benzil with 5-hexenylmagnesium bromide containing 7.4 % of cyclopentylmethylmagnesium bromide, using the standard procedure in (A) ether and (B) THF. (C) Results obtained using equimolar amounts of the reactants in ether.

Product	A	B	C
Benzoin 5-hexenyl ether	61.0	45.8	57.5
Benzoin cyclopentylmethyl ether	3.5	3.3	3.6
α-5-Hexenylbenzoin	30.1	37.5	27.1
α-Cyclopentylmethylbenzoin	5.4	13.4	11.7

branched) in butylmagnesium bromide (straight chain). From the results obtained (see Tables 2 and 3) it was concluded that practically all the cyclic *O*-alkylated product formed arose from the cyclic Grignard reagent, while 70 % of the cyclic *C*-alkylation product was produced by the reaction of straight chain Grignard reagent.

The observation of cyclisation in the *C*-alkyl, but not in the *O*-alkyl product was unexpected. Since the ET mechanism shown in Scheme 1 is assumed to account for both products, the reason for this must be that some of the hexenyl radical has had time to cyclise before combining to form CAP, while combination to the OAP has been immediate.

In the interpretation of the course of the reactions a distinction is made between primary and secondary cage products. The OAP has a geometry very similar to the geometry of the transition state and is formed by direct combination of the radical pair. The secondary cage product is formed with a sligth delay, allowing the alkyl to attack carbon rather than the close-by oxygen.

If the alkyl radical is 5-hexenyl, both primary and secondary cage products are uncyclised, since the rate of cyclisation[9] is 10^5 s^{-1} and the lifetime of the cage is of the order of 10^{-9} s.[10] Cyclised α-cyclopentylmethylbenzoin is formed by escape of the radicals from the cage and re-encounter after a period long enough to allow cyclisation to take place. Since the benzil magnesium ketyl may react with either the excess Grignard reagent to form benzoin or with alkyl radical to form *C*-alkylbenzoin, the relative yield of cyclopentylmethylbenzoin increases when there is no excess of Grignard reagent (Table 3).

It is interesting to compare the results obtained for benzil with the results obtained by Eberson and Greci in an investigation of the reaction of 5-hexenylmagnesium bromide with a phenyliminoindole.[11] The reaction types and the interpretations are closely analogous to those presented above.

The reason why THF leads to more secondary cage product may be that there is a strong coordination of the solvent to magnesium and consequently a "looser" transition state.

In a recent paper, Maruyama and Katagiri give ESR evidence for an ET mechanism in the reaction of benzil with Grignard reagents in THF. This mechanism is characterized by the formation of stable aggregates of anion radicals of benzil paired with dimeric counter-cations of the Grignard reagent.[12] Grignard addition to benzil is assumed to result from reaction of the ion radical pair with an extra molecule of Grignard reagent. The authors determined the rate of disappearance of the red benzil anion radical in the presence of phenyl-, methyl- and ethylmagnesium bromide and claim, thereby, to have measured the rate of the addition reaction.

In the present investigation, the rate of the reaction of phenylmagnesium bromide with benzil was determined by the thermographic procedure.[13] The rate was found to be six times higher than the rate of disappearance of the colour ($k_{\text{thermogr.}} \simeq 100$ s^{-1} contra $k_{\text{colour}} = 16.5$ s^{-1}). The colour is therefore almost certainly due to escaped benzil ketyl, and the reaction observed was electron transfer from the Grignard reagent to the anion to form benzoin. Although not found by the Japanese workers, benzoin is actually produced in the reaction and may be isolated by chromatography. The fate of the phenyl radicals is not clear. The Japanese group did not find biphenyl, but they did not look for benzene, which could be formed if phenyl radical abstracts hydrogen from the solvent. In the present work, small amounts of α-phenylethanol were produced when the reaction took place in ether. This product results from the attack of phenyl radical on ether and was not present in the reagent before the reaction with benzil.

An earlier report[14] on the existence of ion radical pairs, including the cation radical of Grignard reagents, was proved to be erroneous,[15,16] and it seems most likely that the lifetime of the cation radical of a Grignard reagent does not even approach 1 millisecond and is certainly not months or years as suggested in Refs. 12 and 14.

Experimental

Materials. Benzil was recrystallized from carbon tetrachloride. Grignard reagents were prepared under nitrogen using commercial alkyl bromides, sublimed magnesium (Dow), and ether or THF distilled from lithium aluminium hydride. The solutions were titrated with standard acid. 5-Hexenylmagnesium bromide was prepared according to Ref. 17.

Standard procedure for the reaction of benzil with

Table 4. ^{1}H NMR spectra (90 MHz, $CDCl_3$) of compounds **2–29**.

Compd. No.	
2	δ7.67 (2 H, m), 7.37 (8 H, broad s), 4.5 (1 H, s), 1.87 (3 H, s)
3	δ 7.90 (2 H, m), 7.27 (8 H, broad s), 5.45 (1 H, s), 3.43 (3 H, s)
4	δ 7.68 (2 H, m), 7.37 (8 H, m), 4.67 (1 H, s), 2.37 (2 H, q, *J* 6.6 Hz 0.83 (3 H, t, *J* 6.6 Hz)
5	δ 8.00 (2 H, m), 7.40 (8 H, m), 5.57 (1 H, s), 3.62 (2 H, m, ABX_3?) 1.27 (3 H, m, ABX_3?)
6	δ 7.68 (2 H, m), 7.33 (8 H, m), 4.11 (1 H, s), 2.97 (1 H, hept, *J* 6.7), 0.92, (6 H, d, *J* 6.7)
7	δ 8.02 (2 H, m), 7.36 (8 H, m) 5.61 (1 H, s), 3.72 (1 H, hept, *J* 6.4 Hz), 1.23 (3 H, d, *J* 6.4 Hz), 1.19 (3 H, d, *J* 6.4 Hz)
8	δ 7.60 (2 H, m), 7.33 (8 H, m), 4.70 (1 H, s), 2.32 (2 H, t, *J* 6.8 Hz), 1.67–0.66 (7 H, m)
9	δ 8.03 (2 H, m), 7.33 (8 H, m), 5.51 (1 H, s) 1.90–0.66 (7 H, m)
10	δ 7.63 (2 H, m), 7.37 (8 H, m), 4.53 (1 H, s) 2.33 (2 H, d, *J* 6.6 Hz) 0.97 (3 H, d, *J* 6.6 Hz), 0.75 (3 H, d, *J* 6.6 Hz)
11	δ 8.00 (2 H, m), 7.33 (8 H, m), 5.45 (1 H, s), 3.33 (2 H, d *J* 6.6 Hz), 1.83 (1 H, m), 0.92 (6 H, d, *J* 6.6 Hz)
12	Mixture of diastereomers: δ 7.98 (2 H, m), 7.44 (8 H, m), 4.24 (0.6 H, s), 3.89 (0.4 H, s) 2.62 (1 H, m), 1.78–0.78 (8 H, m)
13	Mixture of diastereomers: δ 8.22 (2 H, m), 7.38 (8 H, m), 5.60 (1 H, s), 4.19 (1 H, hex), 1.56 (2 H, m), 1.19 and 1.14 (d, 3 H, *J* 6.7 Hz), 0.89 and 0.82 (t, 3 H, *J* 6.7 Hz)
14	δ 8.00 (2 H, m), 7.60 (8 H, m), 4.5 (1 H, s), 1.11 (9 H, s)
15	δ 8.10 (2 H, m), 7.40 (8 H, m), 5.60 (1 H, s), 1.25 (9 H, s)
16	δ 7.75 (2 H, m), 5.7 (1 H, m), 5.1 (2 H, m), 4.17 (1 H, s), 2.9 (2 H, m)
17	δ 7.69 (2 H, m), 7.27 (8 H, m), 4.0 (1 H, s), 3.78 and 3.53 (AB quartet, *J* 14 Hz)
18	δ 7.70 (2 H, m), 7.31 (13 H, m), 4.9 (1 H, s)
19	δ 8.04 (2 H, m), 7.36 (11 H, m), 6.93 (2 H, m), 6.33 (1 H, s)
20	δ 7.87–6.87 (14 H, m), 4.77 (1 H, s), 2.26 (3 H, s)
21	δ 8.05 (2 H, m), 7.70–6.70 (13 H, m), 6.31 (1 H, s), 2.32 (3 H, s)
22	δ 7.75 (2 H, m), 7.30 (14 H, m), 4.92 (1 H, s), 2.33 (3 H, s)
23	δ 8.06 (2 H, m), 7.45 (10 H, m), 7.06 and 6.83 (AB quartet, *J* 8.6 Hz) 6.31 (1 H, s), 2.24 (3 H, s)
24	δ 7.80 (2 H, m), 7.29 (8 H, m), 6.85 (2 H, s) 4.67 (1 H, s), 2.30 (3 H, s), 2.00 (6 H, s)
25	δ 7.92 (2 H, m), 7.33 (8 H, m), 6.71 (2 H, s), 5.88 (1 H, s) 2.20 (3 H, s), 1.90 (6 H, s)
26	δ 7.62 (2 H, m), 7.36 (8 H, m), 5.71 (1 H, m), 4.84 (2 H, m) 2.53–0.82 (8 H, m)
27	δ 8.02 (2 H, m), 7.38 (8 H, m), 5.78 (1 H, m), 5.50 (1 H, m), 4.96 (2 H, m), 3.52 (2 H, t *J* 6.2), 2.17–1.16 (6 H, m)
28	δ 7.68 (2 H, m), 7.36 (8 H, m), 2.58 (2 H, d, *J* 5.8 Hz), 1.94–0.69 (9 H, m)
29	δ 8.02 (2 H, m), 7.39 (8 H, m), 5.48 (1 H, s), 3.41 (2 H, d, *J* 7.0 Hz), 2.36–1.02 (9 H, m)

Grignard reagents. Five ml of a 1 M Grignard reagent were introduced by means of a disposable syringe into an evacuated 50 ml conical flask. A solution of 106 mg of benzil in 5 ml of ether or THF, and 10 ml of a saturated solution of ammonium chloride were then added through the rubber stopper within 1 s at room temperature. The needle of the syringe was left in the rubber stopper to release the pressure. The aqueous layer was removed under flushing with nitrogen and the organic layer was washed once with water. The moist organic layer was evaporated through a hypodermic needle connected to an aspirator, heating the flask finally to 150 °C for 1 min. After cooling, the flask was opened and the contents analysed by NMR, LC, GLC and HPLC. Preparative LC was performed on silica plates, eluting with 8 % ethyl acetate in hexane. R_f values for OAP, CAP and benzoin were typically 0.6, 0.5 and 0.2, respectively.

Besides the experiments with anaerobic work-up, experiments were performed in which the work-up was carried out with the admission of air, leading to the formation of alkyl benzoates and benzoic acid as shown in eqn. (2).

For NMR observation of the unrearranged alkoxyenol formed according to eqn. (1), evaporation was performed at < 40 °C and the residual

ether or THF was removed by repeated addition of CCl_4 followed by evaporation to dryness. A $CDCl_3$ solution was prepared under nitrogen and transferred to an evacuated NMR tube using a syringe and a rubber septum.

HPLC was performed using a 25 cm × 4,6 mm column packed with Nucleosil® 100–5 silica with UV detection at 254 nm. The mobile phase was 2 % ethyl acetate in hexane.

GLC was performed at 200 °C on a Shimadzu gas chromatograph using a 2 m packed glass column (OV-101 silicone). For quantitative evaluation of chromatograms, peak heights were multiplied by peak retention time.

Kinetics. The thermographic procedure was used as described in Ref. 13. Reaction of 0.01 M benzil and 0.20 M phenylmagnesium bromide in THF at 20 °C showed an initial rate constant $k_1 \simeq 100\ s^{-1}$. The reaction was not ideally first-order, but had a slow stage after the initial fast reaction.

^1H NMR spectra (Table 4) were recorded on a Bruker HXE 90 instrument.

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