The Grignard Reagent Formation Reaction of 2-Chloro-1,1,1-triphenylethane Revisited

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The reaction of 2-chloro-1,1,1-triphenylethane (1) with magnesium in THF has been reinvestigated. The reaction produced a dark-red solution and after deuterolysis with D₂O, 1,1,1-triphenylethane (2; 16 %), 2-D-1,1,1-triphenylethane (3; 52 %) and 1,1,2-triphenylethene (4; 26 %) were isolated. Rate constants for phenyl migration in the 2,2,2-triphenylethyl radical were measured directly between 23 °C and 55 °C; the reaction is described by log k = 11.2 - 7.5/2.3 RT [kcal/mol] and the rate constant for rearrangement at 20 °C is

 4.0×10^5 s⁻¹. The combined results support the intermediate formation of radicals in the reaction of chloride **1** with magnesium. The red colour of the reaction mixture, however, indicates the formation of a carbanionic species, which has not yet been identified. The diffusion model for Grignard formation reactions of Garst et al. is in line with the product distribution.

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Introduction

The heterogeneous nature of the Grignard reagent formation reaction^[1] has hampered its mechanistic investigation considerably. Well-known technical problems include the source and purity of the magnesium used and the induction period (that is, the time before the reaction begins to start). Nevertheless, due to extensive experimentation over a very long period of time a generally accepted mechanism of formation is nowadays widely accepted.^[2] The essential steps of this mechanism basically include: (1) a first outersphere single electron transfer (SET) from the magnesium surface to the organic halide RX, thereby forming a radical anion RX⁻ and an electron-deficient magnesium surface (containing Mg⁺ moieties), and (2) cleavage of RX⁻ in the vicinity of the magnesium surface into the radical R⁻ and the halide anion X⁻. However, it is still not established whether the radical anion RX⁻ is a discrete intermediate or merely a transition state. The halide anion X⁻ subsequently combines with Mg⁺ at the positively charged magnesium surface and forms 'MgX. In step (3), the radical R' and 'MgX combine to form the Grignard reagent RMgX (Scheme 1).



Scheme 1.

Without going into great detail, we would like to reemphasise two main mechanistic issues, which still exist today: (a) is the radical R[•], after being formed in step (2), absorbed by the electron-deficient magnesium surface and is it there converted into the Grignard reagent RMgX, or is it freely diffusing in solution and has it to return to the magnesium surface before it is converted into the Grignard reagent RMgX^[2] and (b) is the radical R⁻ subject to a second SET – step (4) – thereby forming a carbanionic species R: as a discrete intermediate which combines with MgX⁺ to vield RMgX [step (5)].^[2a,2e,3] By CIDNP it has been demonstrated that, after its formation, the radical R[•] is – at least in part – freely diffusing and, consequently, *must* return to the magnesium surface, rather than staying absorbed at the surface.^[4a] The second issue (b) is less easily resolved for at least two reasons. First, the formation of the radical R[·] is rate-determining^[4,5] so that the occurrence of other discrete intermediates formed after the formation of the radical R. can only be proven circumstantially, e.g. by the formation of certain side products which are less plausible for a radical mechanism. Second, although we found some substrates



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which allow stabilisation of a carbanionic species, e.g. by delocalisation of the negative charge, and which formed end-products highly indicative for an intermediate $R^{-,[3]}$ such an intermediate may not be involved in the Grignard reagent formation reaction in general, in particular for substrates where the formation of the end-products may also be rationalised by the intermediate formation of the radical R[•] only. An example of such a substrate is 2-chloro-1,1,1-triphenylethane (1).

Substrates such as 1 are known to undergo 1,2-phenyl migration under radical-formation conditions^[6] and in reactions with alkali metals, presumably involving carbanionic species.^[7] Furthermore, the Grignard formation reaction of 1 was investigated already in the 1950s by Charlton et al. and by Shoppee;^[8] their experimental results were, however, in contradiction with each other, in particular regarding the question whether 1,2-phenyl migration did occur during the Grignard reagent formation reaction or not. A more indepth investigation was performed by Grovenstein et al. who demonstrated that 1,2-phenyl migration did indeed occur.^[9] However, these authors admitted that their experiments showed considerable variability and provided low yields. In our opinion, one of the main reasons for these results is that they performed their experiments using rather highly diluted solutions of 1 (about 0.035 and about 0.085 M). In this respect it is worth noting that the concentration of the starting halide may have a marked effect on the product distribution.^[10] Grovenstein et al. also performed their reactions in the presence of large amounts of methyl iodide and for a relatively short period of time, and they found, after workup, considerable amounts of unreacted 1.^[9]

Here we report new results obtained on the Grignard reagent formation reaction of 1 in THF at rather high concentrations (about 0.17 M) and relatively long reaction times (at least 24 h).

Results and Discussion

The reaction of 1 with triply sublimed magnesium in THF was difficult to initiate, but after stirring for 24 h at ambient temperature, a dark-red solution was obtained. This was observed when the reaction was performed in normal laboratory glass equipment as well as in completely sealed and evacuated glass apparatus. The formation of a dark-red solution has to the best of our knowledge not been reported before in Grignard reagent formation reactions, and it is in our opinion relevant as will be discussed in more detail below. After deuterolysis with D_2O , a mixture of 1,1,1-triphenylethane (2), 2-D-1,1,1-triphenylethane (3) and 1,1,2-triphenylethene (4) was obtained in almost quantitative yield (Scheme 2).

The molar yields were 16% (2), 52% (3) and 26% (4), which implies a total yield of 94%, based on 1. The structural identity of compounds 2–4 was confirmed by ¹H NMR spectroscopy and mass spectrometry. Independent



Scheme 2.

experiments in completely sealed and evacuated glass equipment revealed that even after at least 175 h, the completely reacted reaction mixture showed no further changes, which implies that the formation of 2 and 4 must have occurred during the reaction between 1 and magnesium. These experiments confirm the findings of Grovenstein et al.,^[9] i.e. that 1,2-phenyl migration does occur during the Grignard reagent formation reaction of 1.

Differences between the Results of Grovenstein et al. and this Work

The differences between our experimental results and those of Grovenstein et al.^[9] are presumably due to different reaction conditions. First of all, Grovenstein et al.^[9] reported relatively low yields and considerable amounts of unreacted starting material 1. Their yields for reactions performed in THF were at best in the order of 40% where we found total yields in the order of 94%. Secondly, they performed most of their reactions for relatively short reactions times (not more than 13 h) and added large amounts of methyl iodide to initiate the reaction (32 mmol of methyl iodide to 7 mmol or 17 mmol of 1).^[9] They also observed the formation of Ph₂CHCH₂Ph (7) [the rearranged Ph₂C(MgCl)CH₂Ph (6) was, like in our experiments, not detected after carboxylation], which we did not find (Scheme 3 and Table 1). Nonetheless, they described 4 as a direct product during this reaction, although its yield could not be established because 4 was also formed from unreacted 1 by GLC analysis under their conditions.[11] Furthermore, Grovenstein et al.^[9] found negligible 1,2-phenyl migration in THF, whereas we found considerable 1,2-phenyl migration in the same solvent. It should be pointed out that Grovenstein et al.^[9] also found considerable 1,2-phenyl migration when the reaction was performed in Et₂O and, importantly, detected rearranged Grignard reagent 6 as evidenced by carboxylation. For illustrative purposes, the results of Grovenstein et al.^[9] found for the reaction of 1 in THF with doubly sublimed magnesium and our results obtained with triply sublimed magnesium are shown in Table 1 [yields for 3 (RMgCl) are based on RCO₂H after carboxylation as isolated by Grovenstein et al.^[9] and on RD after deuterolysis as isolated by us].

Scheme 3.



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Entry	1 ^[a] [M]	Solvent	Molar ratio CH ₃ I/1	<i>T</i> [°C]	Reaction time [h]	2 (%) ^[b]	3 (%)	4 (%)	6 (%)	7 (%)	Total yield (%)	Ref.
1	0.085	THF	1.9	45	13	31.0	1.3	[c]	0	5.8	38.1	[9]
2	0.086	THF	1.9	27	3.5	12.7	22.0	[c]	0	1.2	35.9	[9]
3	0.17	THF	0	20 ^[d]	24	16	52	26	0	0	94	this work

[a] Doubly sublimed magnesium (Entries 1 and 2) or triply sublimed magnesium (Entry 3). [b] Calculated as molar yield, based on 1. [c] The combined yield of 1 and 4 was reported to vary between 4 and 16%; cf. ref.^[9] [d] This indicates "ambient temperature".

Are Radicals the Only Intermediates?

Garst et al.^[2d,5] established that, assuming that the diffusion model for the Grignard reagent formation applies, the amount of isomerisation of R[•] is very well approximated by the square-root law known for scavenging radicals or ions:

$$A = \frac{[RMgX]}{[RMgX + Q]} = \frac{1}{1 + (k_Q \tau_R)^{0.5}}$$

where [RMgX] represents the concentration of the formed Grignard reagent, [Q] represents the concentration of products formed by isomerisation (and solvent attack, provided that the rate of solvent attack is slow, i.e. a factor of \geq 10^2 slower, compared to the rate of formation of the actual Grignard reagent RMgX from R⁻ and from the isomerised R', also denoted as Q'), $k_{\rm Q}$ is the rate constant for radical rearrangement, and $\tau_{\rm R}$ is the lifetime for the radical reacting to give the Grignard reagent. Figure 3 of ref.^[2d] indicates for 1 a fractional yield A in the range of about 0.66 to 0.83, which implies that $k_{\rm O} \approx 1.4-8.9 \times 10^5 \, {\rm s}^{-1}$ (when $\tau_{\rm R}$ = 3×10^{-7} s). Our results confirm this: the rearranged product 4 is formed in 26% yield, whereas product 3 (formed from the expected non-rearranged Grignard reagent 5) is 52%, so that the fractional yield A would be 0.67 and $k_{\rm Q} \approx$ $8.1 \times 10^5 \text{ s}^{-1}$ (when $\tau_{\text{R}} = 3 \times 10^{-7} \text{ s}$).

Garst et al. also provided an extended diffusion model, which takes all usual side reactions into account.^[2d,12] This model is characterised by three (scaled) independent parameters V, Δ and $G^2 - 1$: $V = [4k_C/3(k_S^3D)^{0.5}]v$, $\Delta = (Dk_S)^{-0.5} \delta$, $G^2 - 1 = k_C/k_S$.

The parameter V is the (scaled) reaction flux and is a measure for the rate of the formation of R[•] at the magnesium surface; parameter Δ is the (scaled) surface reactivity and is a measure for the rate of the conversion of R[•] at the magnesium surface into RMgX, whereas parameter $G^2 - 1$ is the (scaled) isomerisation rate constant. In these equations, $2k_{\rm C}$ is the rate constant for radical/radical reactions, $k_{\rm S}$ is the rate constant for H-atom abstraction from solvent, $k_{\rm Q}$ is the rate constant for isomerization of the initial radical, v is the radical formation flux, δ is the heterogeneous rate constant for reaction of the radical to give RMgX, and D is the diffusional coefficent.

In the extended diffusion model, it is further assumed that radical R[•] and the rearranged radical Q[•] are converted into their respective organomagnesium compounds at the same rate. Garst et al.^[2d,12] showed that this model is in excellent agreement with the experimentally determined yields of all products accounted for in the reaction of 6-

bromo-1-hexene with magnesium.^[13] In the case of chloride 1, however, the rearranged radical is a relatively stable diphenylalkyl radical, which can react mainly with radical **8** to give products **2** and **4** due to a "persistent radical effect" (a disproportionation reaction discussed in detail later). Therefore, we considered a detailed mechanism for the reaction of **1** with magnesium in THF as depicted in Scheme 4. Radical **8**, produced by reaction of **1** with magnesium, may react by four pathways: reaction with the solvent THF to give **2**; 1,2-phenyl migration to give radical **9**; combination with 'MgCl to give the expected Grignard reagent **5**, which on deuterolysis yields **3**; and disproportionation with radical **9** acting as a reducing agent for **8** to give products **2** and **4**.

$$\begin{array}{c|ccccc} & \underline{Mg, THF} & Ph_{3}CCH_{2}CI \\ 1 & 8 \\ \hline 8 + THF & \underline{k_{S}} & Ph_{3}CCH_{3} \\ \hline 8 & \underline{k_{Q}} & Ph_{2}CCH_{2}Ph \\ \hline 9 \\ 8 & \underline{MgCl} & Ph_{3}CCH_{2}MgCl \\ \hline 5 \\ \hline 8 + 9 & \underline{2k_{C}} & 2 + Ph_{2}C=CHPh \\ \hline 4 \\ \hline 5 & \underline{D_{2}O} & Ph_{3}CH_{2}D \\ \hline 3 \end{array}$$

Scheme 4.

Hence, the rate constants for solvent attack and for phenyl group migration in the 2,2,2-triphenylethyl radical (8) to give the 1,1,2-triphenylethyl radical (9) are necessary for the quantification of the competing processes in the formation of the Grignard reagent ($2k_{\rm C}$ is assumed to be $3 \times 10^9 \,{\rm m}^{-1} \,{\rm s}^{-1}$ as explained below).

Rate Constant for Solvent Attack

The pseudo-first-order rate constant for the reaction of THF with a primary alkyl radical at 50 °C is $k_s = 6 \times 10^3 \text{ s}^{-1}$, which implies that primary alkyl radicals react slowly with THF.^[14] An exception is the cyclopropyl radical $[k_s(\text{THF}) = 7 \times 10^6 \text{ s}^{-1} \text{ at } 25 \text{ °C}]$.^[15] Hence, for radical **8**, a k_s in the order of about 10^3 s^{-1} at ambient temperature seems reasonable which would imply that solvent attack by **8** is a minor pathway for the production of reduced product **2**, which is in agreement with the extended diffusion model when solvent attack can be neglected ($G^2 - 1 > 100$).^[2d,12]

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Rate Constant for Radical Rearrangement

In an early study, Kaplan reported that the phenyl migration in **8** competed with trapping by Ph₃SnH in reactions run at relatively high temperatures and with high concentrations of triphenyltin hydride.^[6c,6e] One can estimate from that work that the rate constant for rearrangement of radical **8** would be in the order of 10^5 to 10^6 s⁻¹ at room temperature, which is a good range for kinetic studies by using Laser Flash Photolysis (LFP) methodology.^[16,17] In order to verify this approximation for k_Q , we measured rate constants for rearrangement of radical **8** directly.

Radical **8** was produced in the LFP studies from the 1-[(3,3,3-triphenylpropanoyl)oxy]pyridine-2(1H)-thione(PTOC)^[18] precursor**10**(Scheme 5), which was prepared byconventional methods from a commercial sample of 3,3,3triphenylpropionic acid.



Scheme 5.

Photolysis of **10** with 355 nm laser light efficiently cleaved the N–O bond to give the pyridin-2-ylsulfanyl radical **(11)** and acyloxyl radical **12**. Decarboxylation of **12** with a sub-nanosecond lifetime gave the target radical **8**, and radical **8** rearranged to radical **9** via **13**, which might be either a short-lived intermediate or a transition state. Alkyl radical **8** has no chromophore absorbing in the range 300–350 nm, but diphenylalkyl radicals such as **9** have strong long-wavelength absorbances centered at ca. 335 nm.^[16] The by-product radical from the photolysis (**11**) has a broad absorbance with $\lambda_{max} = 490 \text{ nm}$,^[19] which can be used to quantify the radical yields. In the LFP experiments, one observes decay of the signal from radical **11** and growth of the signal from radical **9** (Figure 1).

The measured rate constant for signal growth from the reaction of radical 8 in THF at ambient temperature was $k_{\rm obsd.} = 4 \times 10^5 \, {\rm s}^{-1}$. This value is the sum of the rate constants for all reactions that consume radical 8, but several potential interfering reactions cannot be important given the observed rate constant. The concentrations of PTOC ester precursors used in LFP studies are small ($< 10^{-4}$ M), and the rate constant for reactions of a primary alkyl radical with a PTOC ester at room temperature is $k \approx 2 \times 10^6 \text{ m}^{-1} \text{ s}^{-1}$.^[20] The pseudo-first-order rate constant for the reaction of THF with radical 8 at ambient temperature is in the order of 10^3 s^{-1} as explained above. Rates of radical/radical reactions and reactions of radicals with residual oxygen in the LFP studies have pseudo-first-order rate constants in the order of 10⁴ s⁻¹ at most.^[21] Thus, any interfering radical reaction was expected to be too slow to



Figure 1. Time-resolved UV/vis spectrum from the reaction of radical 8. The signal growing at 335 nm is from radical 9, and the decaying signal at 490 nm is from radical 11. The time slices are at 0.9, 1.6, 2.8, 4.5, and 12 μ s. The inset shows the kinetic trace at 335 nm.

be important in the kinetic measurement. This expectation was confirmed by the observation that the signal growth at 335 nm from radical **9** relative to the instantaneous signal at 490 nm from radical **11** was $\ge 90\%$ of the expected value for a diphenylalkyl radical.^[21]

Rate constants for the rearrangement of radical 8 in THF were measured over the temperature range of 23 °C to 55 °C, and the results are shown graphically in Figure 2. The Arrhenius function for the rearrangement is:

 $\log k = (11.2 \pm 0.2) - (7.5 \pm 0.3)/2.3 RT [kcal/mol]$

where the errors are at 2σ . This function gives a rate constant of $4.0 \times 10^5 \text{ s}^{-1}$ for the rearrangement at 20 °C, in good agreement with the results from Kaplan's study.^[6c] The rearrangement of radical **8** is about 500 times faster at room temperature than the phenyl migration in the neophyl radical (i.e. the 2-methyl-2-phenylpropyl radical), but the preexponential terms in the Arrhenius functions (the entropic terms) for the two reactions are quite similar.^[22]



Figure 2. Rate constants for the rearrangement of radical **8**. The line is the Arrhenius function given in the text.

When the LFP study was performed on a long time scale, decay of the signal from radical **9** could be monitored. The observed apparent first-order rate constant was $k_{obsd.} \approx 6 \times 10^3 \text{ s}^{-1}$, which undoubtedly reflects the rates of radical/radical reactions and reactions of radical **9** with residual oxygen. The relatively stable radical **9** provides an important source of hydrogen atoms for the reaction with radical **8** because radical/radical disproportionation reactions will

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have low activation energies and occur with diffusion-controlled rate constants. We expand on this feature in the next section.

Radical Intermediates

According to Garst et al.,^[2d,12] the boundary condition for neglecting solvent attack is $G^2 - 1 > 100$, which condition is fulfilled in the reaction of 1. Thus, solvent trapping of radical 8 cannot produce significant amounts of the reduction product 2. An alternative source of 2 is the reduction of radical 8 by radical/radical disproportionation reactions, and the major source of a "radical-reducing agent" for radical 8 is the relatively stable diphenylalkyl radical 9. The absence of substantial amounts of both the rearranged Grignard reagent 6, Ph₂C(MgCl)CH₂Ph, and the reduction product of radical 9, 1,1,2-triphenylethane (7), indicates that radical 9 accumulated to significant concentrations during the reaction with magnesium. Under those conditions, radical 9 became a persistent radical, and the products formed by radical/radical reactions were controlled by the "persistent radical effect" as described by Ingold and Fischer.^[23,24]

Radicals typically react with one another with diffusioncontrolled rate constants. The persistent radical effect is obtained when self-termination reactions of one radical have barriers due either to steric hindrance or inherent stability of the radical relative to its dimer product. Under those conditions, the concentration of the persistent radical becomes higher than those of other radical intermediates. Because reactions of the persistent radical with other radicals still have diffusion-controlled rate constants, cross-termination reactions of other radicals with the persistent radical become the only important processes for those radicals due to concentration differences. In the context of the current study, we conclude that rearranged radical 9 reacted as a reducing agent for radical 8, which was the only significant reaction channel for 9. This sequence resulted in consumption of a second radical 8 for each rearranged radical 9 formed and thus was the main source of reduction product 2. This conclusion is reinforced by the observation that similar amounts of reduction product 2 and rearrangement product 4 were obtained.

When radical isomerisation occurs in the Grignard reaction but solvent attack is negligible, the product distribution is governed by:^[2d,12]

$$V_Q = [4k_C / 3(k_Q^{3}D)^{0.5}] \mathbf{k}$$
$$\Delta_Q = (Dk_Q)^{-0.5} \delta$$

The parameter V_Q (reaction flux term) is 28.9 and the parameter Δ_Q (surface reactivity term) is 8.7 (boundary condition $G^2 - 1 = 100$).^[25] From these values, one calculates a theoretical fractional yield of $A = V_Q/(V_Q + \Delta_Q) = 0.77$, where the experimental fractional yield is [3]/([3] + [4]) = 0.67. Thus, the experimental values are in reasonable agreement with the extended diffusion model for Grignard for-

mation reactions of primary alkyl halides since the predicted yield of **3** is about 45% (found: 52%) and the predicted yield of rearranged product is about 21% (\approx average of the yields of **2** and **4**).^[12,25]

Are Carbanions Involved?

A definitive answer to this question cannot be given because radical formation is rate-determining as indicated above. However, evidence has been provided for the occurrence of carbanionic intermediates.^[2a,2d,3] In the present case, the dark-red colour of the reaction mixture may be indicative for a carbanionic species.

The reaction between 1 and sodium in refluxing dioxane also produces a dark-red colour; the products found are 2,2,2-triphenylethylsodium (corresponding to 5), 1,1,2-triphenylethylsodium (corresponding to 6), and a small amount of 2.^[7a] The reaction between 1 and sodium in liquid ammonia produces 2,2,2-triphenylethylsodium, 1,1,2-triphenylethylsodium as well as appreciable amounts of 4.^[7c] The formation of the side products is accounted for by the intermediate formation of a carbanionic species. Hence, there may be a similarity between the reaction of 1 and alkali metals and the reaction of 1 with Mg.

Ionisation of Grignard reagents has been reported.^[26] It appears to be strongly dependent on the concentration of the Grignard reagent (> 0.1 M) and on the polarity (dielectric constant ε) of the solvent. Addition of a very polar solvent such as HMPT ($\varepsilon = 31.3^{[27]}$) to solutions of benzyltype Grignard reagents in Et₂O or THF induces ionisation and a bathochromic shift of λ_{max} . Although we conducted experiments at a concentration of 1 in THF of about 0.17 M, it seems unlikely that ionisation of 5 accounts for the observed dark-red colour; note that we did not find 6. In fact, diphenylmethylmagnesium bromide in Et₂O is colourless ($\lambda_{max} = 298 \text{ nm}^{[26a]}$) and the observed λ_{max} for the colourless solution of triphenylmethylmagnesium bromide in Et₂O (318 nm^[26a]) is presumably due to impurities rather than to ionisation of an organomagnesium compound.^[26a] Upon addition of 2 mol-equiv. of HMPT (based on RMgX), a bathochromic shift and a red colour is observed (for diphenylmethylmagnesium bromide: λ_{max} = 323 nm;^[26b] diphenylmethylpotassium in liquid ammonia has a λ_{max} of about 440 nm^[28]). This trend is similar to that observed for the corresponding alkali metal compounds (Li, Na, K, Cs). Consequently, we feel that the dark-red colour observed in the reaction of 1 and magnesium in THF is indicative of a carbanionic species.

On the other hand, it has been reported that under special circumstances, organometallic compounds with lithium or magnesium formally σ -bonded to carbon may show intensive colours for which a clear rationale has not been presented.^[29]

Conclusions

The reaction of 1 and Mg in THF produces the expected Grignard reagent, although 1,2-phenyl migration occurs

and solvent attack can be neglected. The rate constant for phenyl migration in the 2,2,2-triphenylethyl radical **8** is described by $\log k = 11.2 - 7.5/2.3 RT$ [kcal/mol], and the rate constant for rearrangement at 20 °C is $4.0 \times 10^5 \text{ s}^{-1}$. The (extended) diffusion model for Grignard reagent formation reactions is consistent with our experimental results. During the reaction, a dark-red solution is formed which may be indicative for the intermediate formation of a carbanionic species.

Experimental Section

2-Chloro-1,1,1-triphenylethane (1): Compound **1** was prepared from triphenylmethylsodium and dichloromethane according literature procedures.^[7a] After crystallisation from hexane, white crystals of **1** were obtained in 51 % yield (35 %^[7a]). M.p. 99 °C (101 °C^[7a]). ¹H NMR (90 MHz, CDCl₃, 25 °C): $\delta = 4.64$ (s, 2 H, CH₂), 7.05–7.23 (m, 15 H, arom.) ppm. MS: m/z (%) = 292 (1) [M⁺], 256 (22), 243 (100), 178 (13), 165 (50).

Reaction of 1 with Mg in THF: A mixture of 1 (500 mg, 1.7 mmol), triply sublimed Mg (410 mg, 17.1 mmol) and THF (10 mL) was vigorously stirred at room temperature for 24 h, whereafter a darkred solution was obtained. On addition of D₂O, the dark-red colour disappeared immediately, whereupon a saturated aqueous solution of ammonium chloride and Et₂O were added. The organic fraction was separated, and the aqueous fraction was extracted with Et₂O. The organic fractions were combined, washed with water and dried with anhydrous MgSO4. The solvent was evaporated leaving a white solid (445 mg). The product distribution was determined by ¹H NMR analysis (250 MHz, CDCl₃, 25 °C, pulse delay 15 s). Compound 4 was separated from 2 and 3 by preparative GLC: 1,1,1-Triphenylethane (2). Yield: 16%. ¹H NMR $(250 \text{ MHz}, \text{CDCl}_3, 25 \text{ °C})$: $\delta = 2.17 \text{ (s, 3 H, CH}_3), 7.05-7.08 \text{ (m, 6)}$ H, arom.), 7.19–7.24 (m, 9 H, arom.) ppm. MS: m/z (%) = 258 (11) [M⁺], 243 (100), 165 (30).^[30] 2-D-1,1,1-triphenylethane (3). Yield: 52%. ¹H NMR (250 MHz, CDCl₃, 25 °C): δ = 2.15 (br. s, v_{1/2} = 4 Hz, 2 HCH₂), 7.05-7.08 (m, 6 H, arom.), 7.19-7.24 (m, 9 H, arom.) ppm. MS: m/z (%) = 259 (11) [M⁺], 243 (100), 165 (39). Triphenylethene (4). Yield: 26%. ¹H NMR (250 MHz, CDCl₃, 25 °C): δ = 6.88 (br. s, 1 H, CH), 6.91–6.96 (m, 2 H, arom.), 6.99– 7.06 (m, 3 H, arom.), 7.09-7.16 (m, 2 H, arom.), 7.19-7.28 (m, 8 H, arom.) ppm. MS: m/z (%) = 256 (100) [M⁺], 241 (22), 240 (14), 239 (23), 179 (24), 178 (40), 165 (13).^[31] This experiment was repeated in completely sealed and evacuated glass apparatus, wherein the dark-red solution was also formed and remained even after months. Samples were taken and analysed by ¹H NMR spectroscopy and GC-MS after 29 h, 53 h and 175 h. However, the product distribution of all samples was identical within experimental error.

1-[(3,3,3-Triphenylpropanoyl)oxylpyridine-2(1*H*)-thione (10): 1-Hydroxy-1*H*-pyridine-2-thione (0.51 g, 4.00 mmol) and 1,3-dicyclohexylcarbodiimide (0.83 g, 4.00 mmol) were dissolved in dichloromethane (50 mL). The flask was shielded from light, and 3,3,3triphenylpropionic acid (1.10 g, 3.64 mmol) was added. The mixture was stirred for 2.5 h, after which it was washed sequentially with 10% NaHCO₃ solution and brine. Drying with Na₂SO₄, solvent removal by rotary evaporation, and chromatography on silica gel (3:1, hexanes/ethyl acetate) provided the PTOC ester as a light yellow solid (1.11 g, 74%). ¹H NMR: δ = 4.16 (s, 2 H), 6.42 (td, *J* = 6.5, 1.5 Hz, 1 H), 6.60 (dd, *J* = 7.0, 1.0 Hz, 1 H), 7.09 (td, *J* = 6.5, 1.5 Hz, 1 H), 7.24 (m, 4 H), 7.29 (m, 11 H), 7.61 (dd, *J* = 8.5, 1.5 Hz, 1 H) ppm. ¹³C NMR: δ = 43.9, 55.9, 112.4, 126.7, 128.1, 129.2, 133.5, 137.2, 137.5, 145.7, 166.3. 175.8 ppm.

Kinetic Studies: The laser flash photolysis method was the same as described previously.^[16,21] Thus, THF solutions containing PTOC ester **10** in a thermostatted addition funnel were purged with helium to remove oxygen. The solutions were allowed to flow through a reaction cell and were irradiated with 355 nm laser light, and the reaction was monitored at varying wavelengths. The individual runs were collected to generate the time-resolved UV/Vis spectrum of the reaction shown in Figure 1. Kinetics were determined by fitting the growth of signal at ca. 335 nm to a single exponential growth function.

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