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Mechanisms of the Reactions of Grignard Reagents. XIII. Single Electron Transfer in the Reduction of Azobenzene and Benzophenone

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Reaction rate correlations, product distributions, kinetic isotope effects and the use of radical probes in the reaction of azobenzene with a series of Grignard reagents indicate a single electron transfer (SET) as the rate-controlling step. For Grignard reagents carrying a β-hydrogen, the mechanism is suggested to involve a 'β-hydrogen relayed' six-center SET followed by either reaction of the radicals within the cage or reaction after escape from the cage. For Grignard reagents devoid of β-hydrogen a four-center SET is suggested. Both four- and six-center mechanisms may apply to the similar reactions of benzophenone.

The possibility of spin correlation in the radical pair as a factor determining the product distribution is discussed. The application of a magnetic field has no effect on reaction rates or product distributions.

The reaction of benzophenone with Grignard reagents in diethyl ether has been suggested to take place *via* an initial transfer of an electron (SET) to the substrate.[1] In order to obtain more information about the mechanism of the reaction of compounds, which because they have a low reduction potential would likewise be expected to react by typical SET, an analysis of reaction rates and product distributions was made using azobenzene and a series of Grignard reagents.

Earlier investigations had shown that the main products from the reaction of RMgX with azobenzene were hydrazobenzene and hydrocarbons resulting from coupling or dis-

Table 1. Pseudo-first-order rate constants and product distributions (see text) for the reaction of 0.1 M azobenzene with 0.5 M alkylmagnesium bromide in diethyl ether at 20 °C. Number of experiments given in parentheses.

Alkyl	% Addition product	k_{obs} s^{-1}
CH_3	14	$(1 \pm 0.5) \times 10^{-5}$ (3)
C_2H_5	10	$(1 \pm 0.4) \times 10^{-2}$ (3)
Iso-C_3H_7	14	1 (1)
C_4H_9	15	$(2 \pm 0.4) \times 10^{-3}$
Iso-C_4H_9	22	$(1 \pm 0.5) \times 10^{-4}$ (3)
sec-C_4H_9	12	6×10^{-1} (1)
tert-C_4H_9	55	5×10^{-2} (1)
C_3H_5 (allyl)	100	120 (1)
$C_6H_5CH_2$	57	$(3 \pm 1) \times 10^{-4}$ (3)
C_6H_5		1×10^{-5} (1)
$CH_3CH=CHCH_2MgBr$	100	13 (1)
$CH_3CH=CH-CH(MgBr)CH_3$	100	50 (1)

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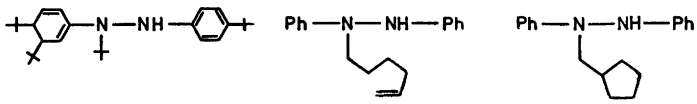


Scheme 1. 1 2 3

proportionation of the alkyl of the Grignard reagent.[2,3]

In the present investigation it was found that, though hydrazobenzene was often the main product, addition products were always present. The crude ratio addition/reduction was obtained by inspection of the NMR spectra of the reaction mixtures. The results are given in Table 1, which also shows reaction rates as obtained by various procedures (see Experimental). It is seen that addition is the dominating reaction when using allylic and benzylic reagents and also using *tert*-butyl Grignard reagent.

A closer investigation showed that several types of addition products were formed. For example, the following products were obtained in the reaction of azobenzene with *tert*-butylmagnesium chloride: hydrazobenzene 50 %, *N*-*tert*-butylhydrazobenzene 20 %, 4-*tert*-butylhydrazobenzene 10 %, 4,4'-di-*tert*-butylhydrazobenzene 7 %, and 3 % of a compound showing *m/e* 410, assumed to be a tetra-*tert*-butyldihydrohydrazobenzene, as for example *1*, Scheme 1.

Experiments with ethyl-, butyl- and *sec*-butylmagnesium bromide showed that *N*- and *C*-monoalkylhydrazobenzenes are formed besides small amounts of dialkylated products (Table 2). The dominating product, when using secondary and primary Grignard reagents is, however, hydrazobenzene.

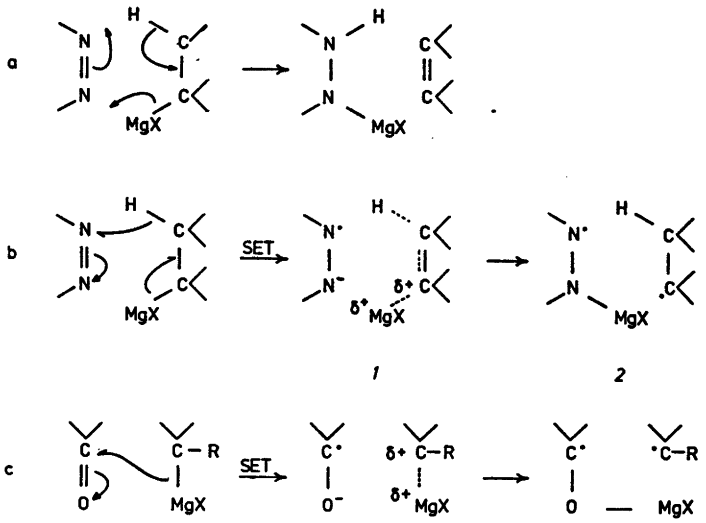
The formation of the various addition products using *tert*-butyl reagent may be explained by the operation of radical mechanisms. Thus, addition of a free *tert*-butyl radical to a *para* position of azobenzene will produce a resonance stabilized radical, which may receive a second *tert*-butyl radical in the *p'*-position. The species obtained may either rearrange to *p,p'*-di-*tert*-butylhydrazobenzene or, since it is still highly conjugated, it may add to two more *tert*-butyl radicals to form, after rearrangement, the tetraalkylated dihydrohydrazobenzene mentioned above.

Formation of 1,2- and 1,6-addition products when using a primary reagent also seems to occur by a radical mechanism. When 5-hexenylmagnesium bromide was used as probe,[4] the 1,2-addition product isolated was more than 50 % cyclized to *N*-cyclopentylmethylhydrazobenzene *2* and *3*, Scheme 1. 1,2- and 1,6-addition products are thus probably formed by the combination of an alkyl radical and a magnesiumhydrazyl radical, both formed by an initial SET. The SET produces the radicals in a solvent cage and combination within the cage produces uncyclized monoalkylated products. Diffusion of radicals out of the cage produces free radicals which may either attack neutral azobenzene (and produce dialkylated products *etc.* as described above) or attack magnesiumhydrazyl radical and produce cyclized 1,2- or 1,6-addition products.

Table 2. Approximate yields of reduction product (hydrazobenzene) and various addition products, alkylhydrazobenzenes, in the reaction of azobenzene with alkylmagnesium bromide in excess. From NMR of the crude product.

R	Hydrazobenzene	1,2-Addition	1,6-Addition	*p,p'*-Dialkylated
Ethyl	80	10	~0.5 [a]	0.1 [a]
Butyl	70	10	2 [a]	–
sec-Butyl	80	10	2 [a]	1 [a]
tert-Butyl	50	20	10	7

[a] Inferred from chromatographic data.



Scheme 2. a. Concerted reduction mechanism as suggested by Whitmore.[6] b. β-Hydrogen relayed SET and carbon-magnesium homolysis. c. Four-center SET followed by homolysis.

There are indications that some addition product is formed in a radical chain process. The use of butylmagnesium bromide and azobenzene leads to *ca.* 15 % of addition product of which the major part is 1,2 and some is 1,6. In the initial phase of the reaction, however, much higher ratios addition/reduction are obtained (up to 70 % addition). In this initial phase azobenzene is consumed at a significantly lower rate when α-methylstyrene is added, and products resulting from capture of butyl radicals by the styrene are found in the reaction mixture. It was not possible, however, to suppress the addition process completely by the addition of α-methylstyrene.[5]

Two (or more) mechanisms may be visualized for the formation of hydrazobenzene. SET followed by diffusion of the alkyl radical may produce magnesiumhydrazyl radicals which may react with a second molecule of Grignard reagent to form the di-magnesiumsalt of hydrazobenzene. This mechanism is the only possible if the reagent has no hydrogen in the β-position as in methyl, benzyl, and phenyl Grignard reagents. If, however, the Grignard reagent has a β-hydrogen the possibility exists of transfer of this hydrogen to azobenzene by the Whitmore mechanism, Scheme 2a.[6] When attached to nitrogen the hydrogen becomes acidic and is removed by a second molecule of Grignard reagent. That a hydrogen atom is actually transferred from the β-position and removed again was shown by the following experiment. One mmol of azobenzene was dissolved in 4 mmol of ethereal phenylmagnesium bromide with which it reacts very slowly ($t_{\frac{1}{2}} > 12$ h). After the addition of one mmol of *sec*-butylmagnesium bromide all azobenzene reacted within 3 min. NMR showed that almost one mol of benzene was produced for every mol of azobenzene consumed. When the same experiment was performed using the primary Grignard reagent β-deuterioisobutylmagnesium bromide the reaction required several hours, but 20 % of the benzene produced contained deuterium.[7]

The fact that hydrogen is transferred from the reducing Grignard reagents does not, however, rule out that SET is involved in the reduction of azobenzene. Especially two facts should be noted, both indicating the operation of SET. It is significant that, although the total reaction rate varies exceedingly, addition seems to be an obligate side reaction (Table 1). The rate of reaction of isopropylmagnesium bromide with azobenzene is 10^4 times faster than that of isobutylmagnesium bromide, but the ratio addition/reduction is almost the same indicating that the factors which increase rate are common for the two reactions and that the mechanisms probably are closely related.

An even more important indication of SET

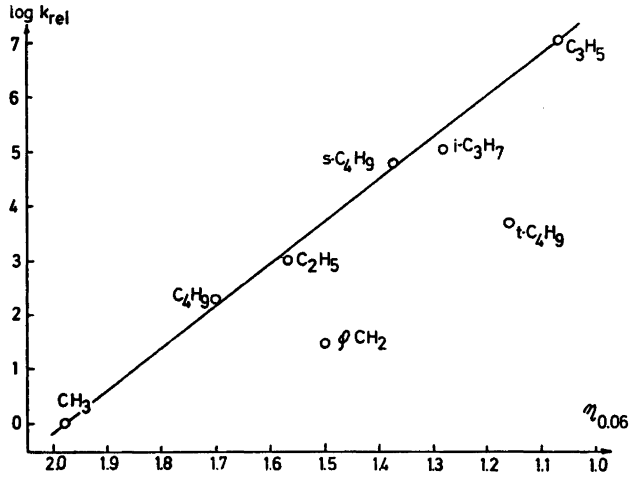


Fig. 1. log (k_{RMgBr}/k_{CH_3MgBr}) for the reaction of Grignard reagents with azobenzene (Table 1) as a function of the anodic oxidation potential $\eta_{0.06}$ (in volt).[8]

is, however, the correlation of log k_{rel} for the reaction between azobenzene and a Grignard reagent, with the anodic oxidation potential for the reagent, shown in Fig. 1. Uncorrelated are the slowly reacting benzyl- and *tert*-butylmagnesium bromides.

The two facts that SET-produced free radicals accompany the reaction to the same extent with fast and with slow reagents and that the reaction rate is correlated with the ease with which the reagents give up a single electron make it necessary to devise a mechanism which is rate controlled by SET, and which to a large extent leads to transfer of β-hydrogen. A proposal is shown in Scheme 2b in the form of a 'hydrogen relayed' SET in which the single electron is donated from the carbon-hydrogen bond, while a pair of electrons are simultaneously shifted from the azo linkage. This leads to a pair of radical ions *1*. Homolysis of the electron deficient C—Mg bond and transfer of magnesium ion yield a caged radical pair *2*, which may collapse to the reduction product, but which may also to some extent diffuse out of the cage to form a pair of free radicals. Reagents which have no β-hydrogen, and for steric reasons also *tert*-butyl, react by a four-center SET which is less efficient. Allylmagnesium bromide, however, has the expected reactivity. In this case the SET may be relayed through the allylic system in a six-center mechanism analogous to the hydrogen relayed mechanism, Scheme 2b.

Like azobenzene, benzophenone seems to react with Grignard reagents by SET since a correlation is possible between log rate and anodic oxidation potential.[8] Furthermore, log k_{rel} for both substrates may also be correlated linearly with the number of β-hydrogens in the Grignard reagent, Fig. 2. In the reaction with azobenzene the rate increases by a factor 10

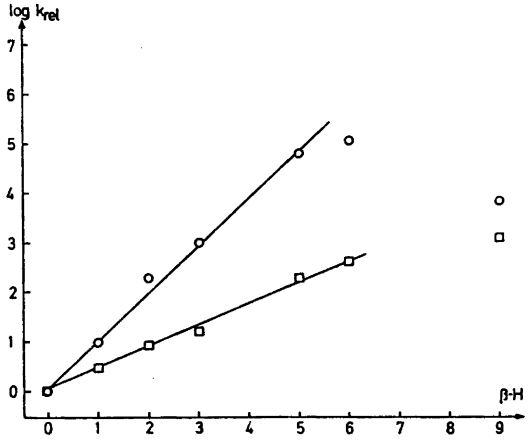


Fig. 2. Ordinate: log (k_{RMgBr}/k_{CH_3MgBr}) for the reaction of RMgBr with azobenzene (○) and benzophenone (□). Rate constants are k_{obs} for the reaction of 0.1 M substrate with 0.5 M Grignard reagent in diethyl ether at 20 °C. Abscissa: The number of hydrogen atoms in the β position in the Grignard reagent: methyl: 0, isobutyl: 1, butyl: 2, ethyl: 3, *etc.*

Table 3. Approximate percentages of C_4 gases produced in the reaction of *sec*-butylmagnesium bromide with excess substrate. Found by GLC of the vapor above the reaction mixture before work up.

Substrate	Butane	1-Butene	*trans*-2-Butene	*cis*-2-Butene	1-Butene/2-Butene
$C_6H_5N=NC_6H_5$	53	37	3	7	3.85
$(C_6H_5)_2CO$	9	41	32	18	0.82
CF_3CHO	6	45	45	4	0.90
CCl_3CHO	12	31	49	8	0.54
$C_4H_8C(COOEt)_2$ [a]	42	30	15	13	1.07
$CoCl_2$	41	15	30	15	0.34
$((CH_3)_2CH)_2CO$	19	45	22	14	1.25

[a] Diethyl butylidenemalonate.

for every β-hydrogen. For benzophenone the factor is only 2.6. The analogy of the plots obtained with Hammett linear free energy plots may indicate that stabilization by hyperconjugation of the cation radicals, which are produced by SET, is a linear function of the number of β-hydrogens (if this number does not exceed 6). Pursuing the analogy with the Hammett equation, it may be suggested that the very big difference in slope for the two plots indicates that two types of SET are in operation, *e.g.*, a six-center SET for azobenzene and a four-center SET for benzophenone, Scheme 2c. For reactions of the two substrates with reagents devoid of β-hydrogen, a six-center SET is excluded, and the mechanisms for reaction of benzophenone and for azobenzene should be of the same type. It is in keeping with this theory that the rate increase factor when going from methyl reagent to benzyl reagent, which determines the slope of the plots, is of the same magnitude for azobenzene as for benzophenone.

Further support for the assumption of a six-center SET for azobenzene and a four-center SET for benzophenone was obtained by identification of the alkenes produced when the two substrates were reduced with *sec*-butylmagnesium bromide, Table 3. Other substrates were included for comparison. In the reaction with azobenzene the least stable alkene, 1-butene, was produced in large excess and *cis*-2-butene was in excess over *trans*-2-butene. With benzophenone the butenes were produced in a ratio approaching that expected from consideration of thermodynamic stabilities. A simple interpretation is that β-hydrogen is engaged in the six-center SET and the engaged hydrogen atom is transferred in a very fast reaction. In the four-center SET the hydrogen transfer is an independent and less specific reaction.

The kinetic effect of substituting the β-hydrogen in the Grignard reagent with deuterium was measured for ethyl- and butylmagnesium bromide. The effect was found much greater in the reaction with azobenzene than in the reaction with benzophenone, Table 4. It is obvious that the β-hydrogen is of more importance in the reaction with azobenzene than with benzophenone. Since there is, however, with benzophenone a definite correlation between

Table 4. Kinetic isotope effect k_H/k_D of substituting β-hydrogen of alkylmagnesium bromides with deuterium on the rate of disappearance of the substrate. Yield of reduction product in parentheses.

Substrate	Ethyl	Butyl	*tert*-Butyl	Cyclopentyl	Isopropyl
Azobenzene	1.6 (85)	2.0 (80)			
Benzophenone	1.01 (6)	1.28 (55)	1.0 (0)	2 (100)	1.16 (20)

the magnitude of the deuterium isotope effect and the relative yield of reduction product it seems possible that the product distribution is in this reaction determined by the competition between two types of SET, *e.g.* the six-center and the four-center, and that this competition is controlled mainly by steric factors, the six-center mechanism being favoured in case of bulky groups around the β-hydrogen as in isobutyl. Preference for the six-center SET may also result if the conformation of the Grignard reagent facilitates a *cis* planar arrangement of β-hydrogen, magnesium, carbon 1, and carbon 2, as in cyclopentylmagnesium bromide. It has been shown that the *cis* planar arrangement is a requirement for the reduction of certain ketones.[9–11]

Mechanistic information was also obtained from the identification of the products from the reactions of the title substrates with 5-hexenylmagnesium bromide. Ashby and Bowers [12] found that the 1,2-addition product obtained in the reaction of this reagent with benzophenone was not cyclized to cyclopentylmethylbenzhydrol. Cyclization was seen, however, in the 1,6-addition product obtained when using a tertiary unsaturated Grignard reagent. In the reaction with azobenzene we found *ca.* 50 % cyclization in the 1,2-addition product when using 5-hexenylmagnesium bromide, and cyclization was observed also in the 1,6-addition product.

In their interpretation Ashby and Bowers suggested that 1,2-addition product was produced from a magnesium bound radical, while 1,6-addition product resulted from combination of a free alkyl radical with the magnesium ketyl within a solvent cage. The lifetime of a caged radical pair [13] is assumed, however, to be 10^{-9} to 10^{-10} s while the rate constant for cyclization [14] of the 5-hexenyl radical is 10^{5} s^{-1}. Collapse of the radicals within the cage should, therefore, leave no time for cyclization and observation of cyclization must mean that alkyl radicals have diffused out of the cage and have reacted with free magnesium ketyl radicals.

The reason why radicals should diffuse apart and later react by reencounter is somewhat obscure. One possibility is steric hindrance for the 1,2-addition. Another possibility is that the necessary spin pairing is obtained only after diffusion and reencounter of the radicals. It is reported from a Russian group that an increase in the amount of cage product is obtained when the reaction of benzyl chloride and butyllithium is run in a magnetic field.[15] For this reason the reaction of butylmagnesium bromide and benzobenzene was run in a 15 000 G field with no clear-cut effect on product distribution. Effect was lacking also in the reaction of Grignard reagent with ethyl cinnamate.[5] Attempts to reproduce the results of the Russian workers were, however, also unsuccessful, since identical reaction mixtures were obtained, whether the reaction with benzyl chloride was run with or without a magnetic field.

Summing up, the SET from Grignard reagent to a substrate may have a six-center or a four-center transition state, and the primary cage product resulting from immediate ($< 10^{-11}$ s) collapse of the radicals will reflect the geometry of the transition state. A fraction of the radicals do not collapse immediately, but may collapse to products not reminiscent of the SET geometry or they may diffuse out of the cage and react by reencounter or with radical scavengers (*e.g.* azobenzene, ethyl cinnamate, methylstyrene).

EXPERIMENTAL

Mass spectra were recorded on a V. G. Micromass 7070 F instrument; IP 70 eV. ^{1}H NMR spectra were recorded on a Bruker HXE 90 instrument (90 MHz) and on a Varian 360 instrument (60 MHz). Merck Kieselgel 60 PF_{254} was used for chromatography. Grignard reagents were prepared from sublimed magnesium (Johnson, Matthey Chemicals) using commercial alkyl halides and ether distilled from lithium aluminium hydride. Azobenzene (Fluka AG, *puriss.*) was used without purification. α-Methylstyrene (Roehm & Haas, *puriss.*) was distilled before use.

Kinetics. For slow reactions (methyl, isobutyl, benzyl, phenyl) samples were withdrawn from the thermostated reaction mixture and analyzed by NMR after anaerobic work-up. Integration of the signals from the aromatic protons for azobenzene (δ 7.36 – 8.0), and for hydrazobenzene (δ 6.6 – 7.3), the NH protons of hydrazobenzene (*ca.* δ 4 – 6), and the aliphatic protons of *N*-alkyl and *C*-alkyl groups allowed the determination of azobenzene consumed and of hydrazobenzene and addition products formed. For fast reactions thermographic procedures were used, using a calorimeter [16] or a flow stream arrangement.[17]

The rate constants given in Table 1 are found as 0.7 divided by the first half time in s. The values are approximate and some are reproducible only within ±50 %. The reactions are catalysed by the trace amounts of metals present even in the sublimed magnesium. Handling of the reagents by means of hypodermic needles was avoided if possible because of the risk of copper contamination from the solder.

The reaction of butylmagnesium bromide and azobenzene was followed in UV at the absorption maximum for azobenzene at 320 nm ($\varepsilon \sim 10\,000$). Using a 1 mm cell and a concentration of azobenzene of 10^{-3} M the reaction was found to be approximately first order in azobenzene and first order in Grignard reagent. For 0.50 M Grignard reagent a second-order rate constant of $k = 0.0041$ l s^{-1} mol^{-1} was found at 20 °C. At 30 °C $k = 0.0072$ l s^{-1} mol^{-1}, $E_A = 42 \pm 8$ kJ mol^{-1}, $\Delta S^{\ddagger} = 155 \pm 29$ J °C^{-1} mol^{-1}. In the presence of 4 % v/v of α-methylstyrene the rate constant was lowered to 0.0023 l s^{-1} mol^{-1}. For comparison the presence of 4 % of toluene resulted in $k = 0.0033$ l s^{-1} mol^{-1}.

Free radical capture. Azobenzene (1 g) was reacted with 20 ml *ca.* 1 M butylmagnesium bromide for 3 days in the presence of 1 g of α-methylstyrene. A large white precipitate of hydrazobenzene dimagnesium salt was formed. The supernatant was poured onto cold saturated ammonium chloride. The organic layer was evaporated at 100 °C *in vacuo* to yield a yellow oil (250 mg). NMR showed the presence of hydrazobenzene, *N*-butylhydrazobenzene, and *C*-butylhydrazobenzene (see below). GLC combined with MS showed the presence of 2-heptylbenzene, 2,2-dimethylpentylbenzene, and 2-phenyl-1-heptene. MS, furthermore, indicated the presence of *N*-butylaniline and of *N*-phenyl-*N'*-butylhydrazine, both assumed to be thermal decomposition products.

Product distribution. One g of azobenzene was reacted as above without the addition of α-methylstyrene. Extraction with light petroleum gave 250 mg of a yellow oil. TLC using 5 % ethyl acetate in light petroleum yielded, besides hydrazobenzene, the following fractions: *C*-Butylazobenzene (8 mg, R_F 0.95), ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.8–1.9 (m) and 3.13 (broad t, butyl), 7.2–8.0 (m, aromatic). *N*-Butylhydrazobenzene (98 mg, R_F 0.85; R_F of azobenzene is 0.90), ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.7–1.8 (m) and 3.44 (broad t, butyl), 5.2 (broad s, NH), 6.6–7.3 (m, aromatic). *C*-Butylhydrazobenzene (26 mg, R_F 0.35), ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.7–1.8 (m) and 2.50 (broad t, butyl), 5.04 (broad s, NHNH), 6.6–7.3 (m, aromatic).

Azobenzene (1 g) was added to 20 ml of 1 M etheral *tert*-butylmagnesium chloride. After 15 min the mixture was poured onto cold saturated ammonium chloride, avoiding contact with the atmosphere. The organic layer was evaporated, leaving 1.1 g of an oil which was extracted with 10 ml of light petroleum leaving 0.72 g (71 %) of hydrazobenzene, m.p. 123–125 °C. The extract contained 0.36 g of an oil. 233 mg was separated by TLC using 10 % methyl acetate in light petroleum. The following fractions were collected: Hydrazobenzene (R_F 0.30, 14 mg, m.p. 123–125 °C). 4-*tert*-Butylhydrazobenzene (R_F 0.40, 27 mg, ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.27 (*tert*-butyl), 3.44 (broad, NHNH), 6.7–7.3 (aromatic). 4,4'-di-*tert*-Butylhydrazobenzene (R_F 0.50, 36 mg, m.p. 108–112 °C; lit.[18] 127–129 °C). ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.29 (*tert*-butyl), 5.11 (broad, NH), symmetric dd with separation 9 Hz and gravity centers at δ 6.81 and 7.23 (aromatic), *N*-*tert*-Butylhydrazobenzene (R_F 0.63, 50 mg, m.p. 47–52 °C; lit. 54–55 °C,[19] ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.20 (*tert*-butyl; lit.[19] 1.10), δ 4.5–5.2 (broad s, NH), 6.6–7.2 (aromatic). 4,4'-Di-*tert*-butylazobenzene (R_F 0.90, 7 mg, ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.35 (*tert*-butyl), symmetric dd with separation 8 Hz and gravity centers at δ 7.51 and 7.83 (aromatic).

The same experiment was carried out using a column (Merck Fertigsäule Kieselgel 60) for the separation. Besides the fractions mentioned above, a product eluted after the di-*tert*-butylazobenzene showed an *m/e* at 410.

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