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Catalytic olefination of carbonyl compounds. Effect of the structure of the carbonyl compound on the reaction

V. N. Korotchenko,[a] A. V. Shastin,[b] V. G. Nenaidenko,[a]★ and E. S. Balenkova[a]

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119992 Moscow, Russian Federation.
E-mail: nen@acylium.chem.msu.ru
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
14 Institutskii prosp., 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail shastin@icp.ac.ru

The mechanism of the novel reaction of catalytic olefination of carbonyl compounds was studied. The reaction involves the transformation of hydrazones of aromatic aldehydes and ketones into the corresponding dichloroalkenes and symmetrical azines by the treatment with carbon tetrachloride in the presence of CuCl as a catalyst. The stability of intermediate diazoalkanes is the main factor determining the direction of the reaction. In the case of sufficiently stable diazoalkanes, other products can be formed under the reaction conditions along with the products of catalytic olefination.

Key words: catalysis, copper salts, carbonyl compounds, hydrazones, diazoalkanes, carbenes, alkenes, olefination.

Olefination of carbonyl compounds, being the transformation of the carbonyl group into the double carbon-carbon bond, is one of the most convenient and universal method for the preparation of alkenes.[1] Great diversity and accessibility of carbonyl compounds allows olefination to be used for syntheses of a wide scope of substituted alkenes. The Wittig reaction and its modifications[2] and the synthesis using equimolar amounts of metals as reducing agents[3] are classical approaches to olefination. However, searching for new catalytic routes for this transformation remains important because considerable amounts of phosphorous reagents and/or metals should be usually used and drastic requirements are imposed on the conditions of this reaction.

Results and Discussion

We have recently found the novel catalytic olefination reaction (COR) of carbonyl compounds **1**. It has been shown that *N*-unsubstituted hydrazones **2** of aromatic aldehydes can be transformed into dichloroalkenes **3** by the treatment with CCl_4 in the presence of catalytic amounts of copper(I) chloride (Scheme 1).[4—6] The reaction is accompanied by nitrogen evolution, and alkenes **3** are formed along with symmetrical azines **4**.

The further studies showed that the discovered reaction is of general character, and a wide scope of compounds with the general formula $CHal_2XY$ can be used as olefination agents. For example, CCl_4,[4—7] $CHBr_3$,[7,8] CBr_4,[7,9] and Freons CF_3CCl_3 [10] and $CF_2ClCFCl_2$ [10] can be used as C_1- and C_2-building blocks in syntheses of the corresponding substituted alkenes. We used hydrazones of aromatic and heteroaromatic aldehydes[4—6,8—10] and alkyl aryl ketones[7] as carbonyl components. The method proposed for alkene synthesis has such unambiguous advantages as simplicity of experimental design and isolation of products, mild conditions and easiness of the reactions, and high yields of target products. These features make this reaction very promising and convenient for use in organic synthesis.

The purpose of this work is to study the influence of the structure of carbonyl compounds and their derivatives on the regularities and direction of the reaction. Hydrazones **2a—h** of substituted benzaldehydes and acetophenones were chosen for the study. Substrates with both electron-donating and electron-withdrawing substituents in the aromatic cycle were studied. In the series of hydrazones **2a—h**, steric shielding of the hydrazone group increases on going from aldehydes to alkyl aryl ketones and further to diaryl ketones, which should decrease its reactivity. Unlike the previously studied types of hydrazones, compounds **2g** and **2h** have two aromatic substituents at the carbonyl group. The behavior of such substrates has not previously been studied under the COR conditions.

Hydrazones **2a—h** were treated with CCl_4 chosen as model polyhaloalkane under the standard olefination conditions.[5] The reaction was carried out in DMSO using

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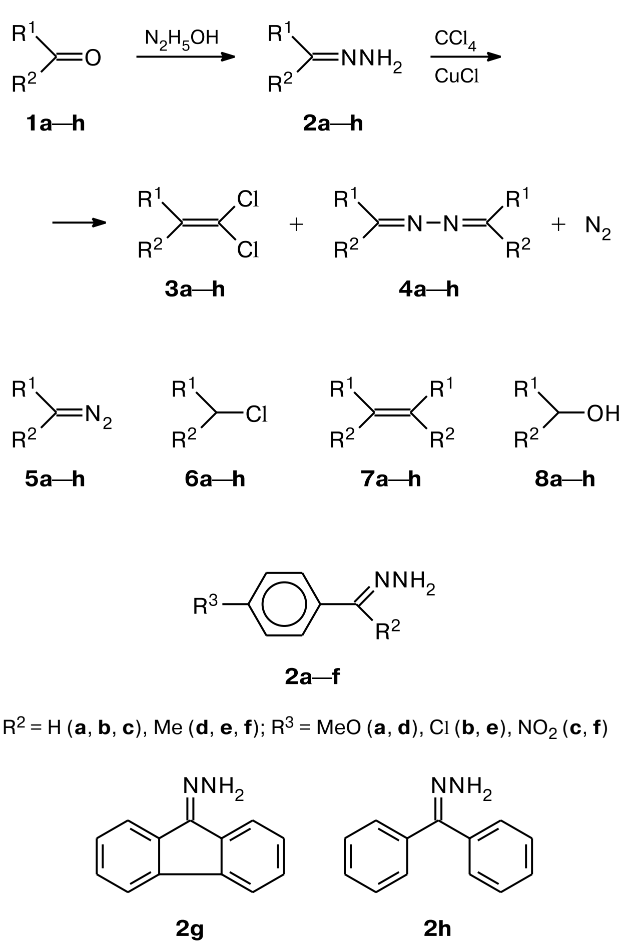
Scheme 1



R^2 = H (**a**, **b**, **c**), Me (**d**, **e**, **f**); R^3 = MeO (**a**, **d**), Cl (**b**, **e**), NO_2 (**c**, **f**)

5 equiv. of CCl_4 in the presence of a base (aqueous ammonia) and 10 mol.% of CuCl as a catalyst. By analogy to the earlier studies of catalytic olefination, we can assume that the main products of transformation of hydrazones **2** are the corresponding dichloroalkenes **3** and symmetrical azines **4** of carbonyl compounds.

Catalytic olefination is accompanied by nitrogen evolution. The reactivity of substrates toward CCl_4 can be estimated by measuring the rate of nitrogen evolution. It turned out (Fig. 1) that in the series of substrates of the same type, *viz.*, hydrazones **2a**—**c** of *para*-substituted benzaldehydes and hydrazones **2d**—**f** of *para*-substituted acetophenones, the enhancement of the donating ability of the substituent in the aromatic ring increases the rate of nitrogen evolution. For example, in the case of hydrazones **2a** and **2d** containing the methoxy group, the rate of nitrogen evolution is maximal. It is seen (see Fig. 1) that in the pairs of substrates **2a** and **2d**, **2b** and **2e**, **2c** and **2f** the rates of gas evolution are close. This fact suggests that in the series of aromatic aldehydes and aryl methyl ketones the electronic factors exert the highest effect on the rate of the reaction of hydrazones with polyhaloalkanes. Steric shielding of the hydrazone group also affects the reaction rate, although to a less extent. For example, for hydrazone **2h** the complete conversion occurs approximately within 30 days (TLC monitoring), while the complete conversion of hydrazones **2a**—**g** takes 3—24 h. This behavior of hydrazone **2h** can be attributed to both the greatest steric shielding of the hydrazone group in this series of substrates and a change in the electronic factors. Based on the obtained experimental data, we found that the rate of transformations of the hydrazones under the COR conditions decreases in the series **2a** ≈ **2d** > **2b** ≈ **2c** ≈ **2e** ≈ ≈ **2f** >> **2g** >> **2h**.

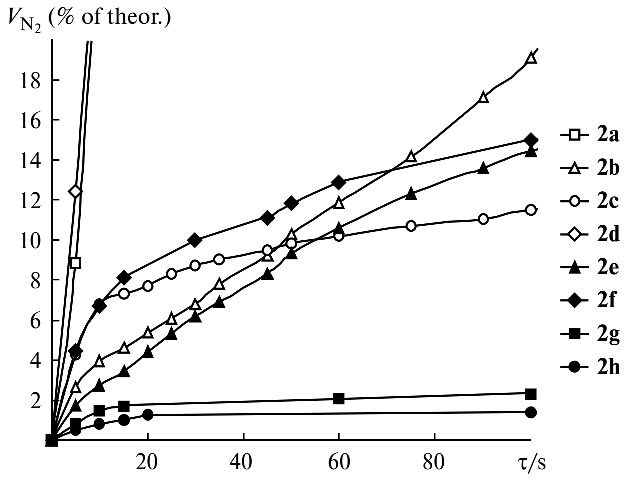


Fig. 1. Nitrogen evolution upon treatment of hydrazones **2a**—**h** with CCl_4 (initial step of the reaction).

We examined in detail the products of transformation of hydrazones **2a**—**h** under the reaction conditions (Table 1). In the case of hydrazones **2a**—**f**, the total yield of two expected products, *viz.*, corresponding dichloroalkenes **3** and *sym*-azines **4**, is almost 100%. However, already for fluorenone hydrazone **2g**, "anomalous" prod-

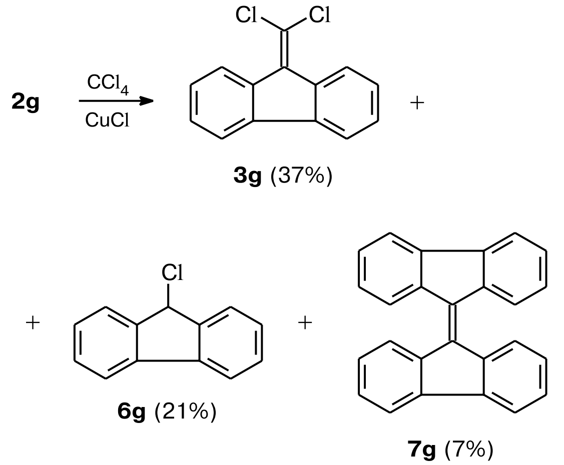
Table 1. Yields (%) of the products of transformation of hydrazones **2a**—**h** under the reaction conditions

Hydrazone	Products			"Anomalous" products
	3a—h	4a—h	3a—h + 4a—h	
2a	49	44	93	—
2b	74	19	93	—
2c	79	17	96	—
2d	88	7	95	**1d***
2e	82	14	96	**1e**,* **7e**,* **8e***
2f	58	32	90	**1f***
2g	37	0	37	**6g** (21), **7g** (7), **1g**,* **8g***
2h	0	0	0	**1h** (37), **8h***

* The product was detected in trace amounts by GLC-MS spectrometry.

ucts, *viz.*, 9-chlorofluorene (**6g**) and 9,9′-bifluorenylidene (**7g**), were obtained along with the expected 9-dichloromethylenefluorene (Scheme 2). The corresponding fluorenone azine **4g** was not isolated.

Scheme 2



3g (37%)

6g (21%)

7g (7%)

In the case of benzophenone hydrazone **2h** (at its 100% conversion), the only isolated product was benzophenone **1h** (37% yield), which forms due to the oxidative cleavage of the C=N bond under the reaction conditions.[11]

Thus, in the case of hydrazones **2a—f**, the results agree well with the assumption, whereas the behavior of hydrazones **2g** and **2h** containing two aromatic substituents does not obey the general scheme of COR.

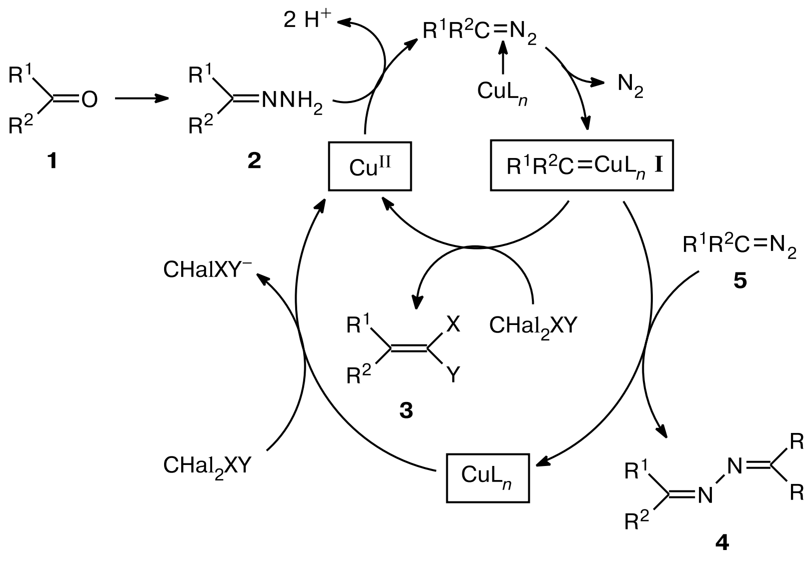
To reveal the dependence of the composition of the formed products on the substrate structure, we studied the products of transformation of hydrazones **2a—h** under the same standard conditions using GLC-MS spectrometry, which detects trace amounts of substances. In the case of aldehyde hydrazones (hydrazones **2a—c**), only products of COR **3a—c** and **4a—c** were found in the reaction mixtures. On going to acetophenone hydrazones (hydrazones **2d—f**), the main products were found along with "anomalous" products: ketones **1d—f**, stilbenes **7d—f**, which are formal products of doubling the corresponding carbenes, and 1-arylethanols **8d—f**. In the case of hydrazone **2g**, the formations of target alkene **3g** and "anomalous" products compete. For substrate **2h**, no products of COR were found in the reaction mixture. However, oxygen-containing products, *viz.*, corresponding ketones **1g**,**h** and alcohols **8g**,**h**, were detected in the GLC-MS spectra of the reaction mixtures in the case of **2g** and **2h**.

Thus, the gradual transition from the substrates that enter into COR to the substrates involved in alternative reactions occurs in the studied series of hydrazones of aromatic carbonyl compounds **2a—h**.

We have previously[6—10] proposed the catalytic cycle describing COR (Scheme 3). In the first step, hydrazone **2** is oxidized by Cu^{II} to form the corresponding diazoalkane **5**. The involvement of diazoalkanes as intermediates of COR has reliably been proved earlier.[5] The subsequent copper-catalyzed decomposition of diazoalkane **5** affords copper-carbene complex **I**, which is the key intermediate of the reaction. The reactions of complex **I** with polyhaloalkanes results in the corresponding dihaloalkenes **3** with regeneration of Cu^{II} and beginning of a new catalytic cycle. In addition to this, complex **I** reacts with diazoalkane **5** to form azine **4**.

The formation of products **1** and **6—8** from hydrazones **2g**,**h** under the reaction conditions cannot be explained by the earlier proposed catalytic cycle. We assumed that

Scheme 3



the difference observed for the behavior of the substrates can be attributed to a change in the steric factors and stability of intermediate diazoalkanes **5**. Diazoalkanes are widely used in the synthetic organic chemistry, and their properties are described in fundamental reviews and monograph.[12] The published data on the enhancement of the thermostability of diazoalkanes and their stability toward decomposition in acidic media in the series alkyldiazomethanes < $PhC(Me)=N_2$ < $PhCH=N_2$ << << $Ph_2C=N_2$ < diazofluorene and on the stabilization of aryldiazoalkanes with electron-withdrawing substituents in the aromatic cycle are available.[12] At the same time, steric shielding of the diazo group increases in the series of diazoalkanes **5** formed from hydrazones studied in this work: $4\text{-}ClC_6H_4C(H)=N_2$ (**5b**) < $4\text{-}ClC_6H_4C(Me)=N_2$ (**5e**) << diazofluorene (**5g**) < $Ph_2C=N_2$ (**5h**). According to the mechanism proposed by us for the transformation of hydrazones **2**, nitrogen is evolved in the reaction medium upon diazoalkane decomposition. The data on the rate of gas evolution can thus correlate with the stability of diazoalkanes under these conditions. As can be seen in Table 1, an increase in the amount of the "anomalous" products correlates with an increase in the stability of diazoalkanes.

To establish the mechanism of formation of products **1**, **6—8**, we scrutinized the transformations of diazoalkanes in the reaction medium for the most stable diazofluorene **5g** and diphenyldiazomethane **5h**. With this purpose, we studied the decomposition of preliminarily prepared diazofluorene **5g** (Table 2) and diphenyldiazomethane **5h** under standard conditions (DMSO as solvent, and aqueous ammonia as base).

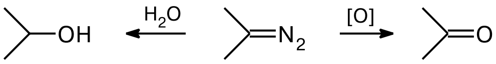
We found that diazofluorene and diphenyldiazomethane slowly decompose with nitrogen evolution upon the treatment with CCl_4 in a DMSO solution in the presence of aqueous ammonia even in the absence of CuCl. Note that the decomposition of diazofluorene **5g** occurs several times more rapidly than the decomposition of diphenyldiazomethane **5h** (according to the data on gas evolution), *i.e.*, under these conditions, diphenyldiazomethane is more stable than diazofluorene.

Fluorenone **1g** (45%) and fluorenol **8g** (30%) are the main reaction products of diazofluorene **5g** transformation (see Table 2). Benzophenone **1h** (41%) was the only product isolated in the case of diphenyldiazomethane **5h**.

Table 2. Yields (%) of the products of decomposition of diazofluorene **5g**

Reaction conditions	Reaction products			
	1g	**7g**	**8g**	**3g** and **6g**
CCl_4 (5 equiv.), without CuCl	45	0	30	—
CuCl (10 mol.%), without CCl_4	0	21	0	—
CuCl (10 mol.%), CCl_4 (5 equiv.)	60	10	0	Traces

These data show that oxygen-containing products can form due to noncatalytic transformations of diazofluorene in the reaction mixture. It is known[12,13] that alcohols and carbonyl compounds are formed from diazoalkanes due to the interaction of the latter with water and oxidants (DMSO, oxygen) present in the system. It is likely that similar processes also occur in this case.



Copper(I) chloride catalyzes the decomposition of diazofluorene **5g** in DMSO in the presence of aqueous ammonia and in the absence of CCl_4. 9,9′-Bifluorenylidene **7g** was isolated as the sole product, which agrees with the published data[14] on the formation of 9,9′-bifluorenylidene due to the decomposition of diazoalkane **5g** catalyzed by compounds of various transition metals, such as copper, nickel, gold, and others.

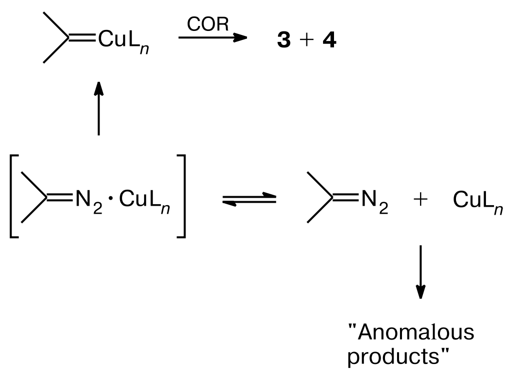
9-Chlorofluorene **6g** forms upon diazofluorene **5g** decomposition as a result of the elimination of the halogen atom from CCl_4 in the presence of CuCl. Halogen atom elimination is characteristic of carbenes generated from diazoalkanes thermally, photochemically, or by transition metal catalysis.[12,15] For example, it is described[15] that photolysis of diazofluorene in chlorine-containing solvents is followed by the chlorine atom transfer and formation of 9-chlorofluorene.

We also studied the decomposition of diazofluorene **5g** under the same conditions in the presence of the copper catalyst and CCl_4. For this process, unlike hydrazone transformations under similar conditions, fluorenone **1g** (60%) is the main product, and 9,9′-bifluorenylidene **7g** (10%) additionally forms. Dichloroalkene **3g** and 9-chlorofluorene **6g** are formed only in trace amounts.

These data agree completely with our proposal that diazoalkanes are involved in the formation of the "anomalous" products and are evident for the effect of the kinetic parameters of the reaction. An increase in the stability of diazoalkanes **5** under these conditions and, as a consequence, a decrease in the rate of copper-carbene complex formation result in the escape of diazoalkane from the catalytic cycle of COR and participation in side reactions, which are both catalyzed by copper salts and noncatalyzed. These data allow us to supplement the catalytic cycle describing COR by another direction: transformation of diazoalkanes into by-products (Scheme 4).

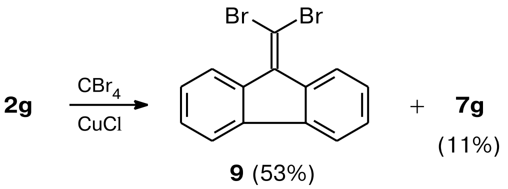
These results evidence that fluorenone exists at the boundary of COR application in this series of carbonyl compounds. This specific feature of fluorenone is very useful for analysis of the effect of various factors on the competition between COR and side reactions of intermediately formed diazofluorene. We assumed that the enhancement of the reactivity of polyhaloalkane should result in an increase in the rate of its reaction with the

Scheme 4



copper-carbene complex and, correspondingly, in the competitive increase in the amount of the COR products over that of by-products. It has previously[7] been shown that the reactivity of CBr_4 is much higher than that of CCl_4 in the series of substrates of the same type under the COR conditions. To check the hypothesis about the critical role of the copper-carbene complex in the reactions with halohydrocarbons, we treated fluorenone hydrazone **2g** with CBr_4 under similar conditions. It turned out that the yield of dihaloalkene increased almost 1.5-fold. 9-Dibromomethylenefluorene **9** and bifluorenylidene **7g** are the main products of this reaction (Scheme 5), which additionally confirms the advanced hypothesis.

Scheme 5



Thus, the relation between the structure of the starting carbonyl compound and its derivatives and the nature of the reaction products was revealed from the experimental data. The ratio of rates of formation and consumption of diazoalkane **5** in the catalytic COR cycle and outside the latter plays the determining role, and the competition of these directions depends on the reactivity of diazoalkane. In the case of formation of lowly stable diazoalkanes from hydrazones of aromatic aldehydes and alkyl aryl ketones, COR is the main process.[4—10] Diazofluorene exhibits the intermediate type of stability, due to which both olefination and noncatalytic transformations of this diazoalkane occur. In the case of diphenyldiazomethane, the COR cycle does not occur. These data substantially deepen our knowledge about the nature of the reaction under study and suggest that COR can be applied to various aromatic aldehydes and alkyl aryl ketones.

Experimental

^1H NMR spectra were recorded on a Varian VXR-400 spectrometer (working frequency 400 MHz) in $CDCl_3$ using Me_4Si as internal standard. The reaction was studied by TLC on Merck $60F_{254}$ plates. Column chromatography was carried out on Merck silica gel (63—200 mesh). GLC-MS spectra were obtained on an HP5890 instrument (EI, 70 eV) using a 5989x-G detector.

Hydrazones **2a—c**,[5] **2d—f**,[7,16] **2g**,[17] and **2h**[18] were synthesized from the corresponding carbonyl compounds according to published procedures. Diazofluorene **5g**[19] and diphenyldiazomethane **5h**[18] were prepared by oxidation of the corresponding hydrazones.

Reactions of hydrazones 2a—h with CCl_4 (general procedure). Aqueous ammonia (1.80 mL) and freshly purified CuCl[20] (50 mg, 0.5 mmol, 10 mol.%) and then one portion of CCl_4 (2.41 mL, 25 mmol) were added to a solution of freshly synthesized hydrazone **2a—h** (5 mmol) in DMSO (5 mL) at 20 °C. The volume of the evolved gas was measured using a gas burette. After the end of the reaction (TLC monitoring), the reaction mixture was poured into water (500 mL). The reaction products were extracted with CH_2Cl_2 (3×50 mL), the combined extracts were dried with Na_2SO_4, the solvent was evaporated, and the reaction products were isolated using column chromatography (SiO_2).

The reaction of hydrazone **2g** with CBr_4 was performed similarly using a solution of CBr_4 (8.30 g, 25 mmol) in DMSO (20 mL).

Decomposition of diazofluorene 5g. Freshly prepared diazofluorene (0.96 g, 5 mmol) was dissolved in DMSO (5 mL). The resulting solution was added by concentrated (25%) aqueous ammonia (1.80 mL). The further treatment was carried out using one of the following methods.

A. One portion of CCl_4 (2.41 mL, 25 mmol) was added to the resulting solution at 20 °C.

B. The solution was added by one portion of CuCl (50 mg, 0.5 mmol, 10 mol.%) at 20 °C.

C. The solution was added by one portion of CCl_4 (2.41 mL, 25 mmol) and immediately by CuCl (50 mg, 0.5 mmol, 10 mol.%) at 20 °C.

After the end of nitrogen evolution, the reaction mixture was treated as described for hydrazones.

Freshly synthesized diphenyldiazomethane **5h** (0.97 g, 5 mmol) was decomposed according to method *A* described for diazofluorene **5g**.

The spectroscopic and physical characteristics of synthesized compounds **1g,h**,[20] **3a—c**,[5] **3d—f**,[7] **3g**,[21] **4a—c**,[5] **4d**,[22] **4e**,[16] **4f**,[7] **6g**,[23] **7g**,[24] **8g**,[25] and **9**[21] agree with the published values.

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