Syntheses of Formazans Under Phase-Transfer Conditions

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Several 1,3,5-triarylformazans were synthesized (42–77%) using a new methodology. Azo-coupling of aryldiazonium salts with arylaldehyde arylhydrazones under mild basic conditions in two-phase liquid-liquid media is efficiently promoted by phase-transfer catalysts (onium salts or dicyclohexano-18-crown-6) at 5–25°C. The condensation of benzaldehyde with phenylhydrazine followed by phase-transfer catalyzed azo-coupling with phenyldiazonium chloride (one-pot procedure) gave 1,3,5-triphenylformazan in a 54% yield without isolation of the intermediate benzaldehyde phenylhydrazone. A double azo-coupling reaction of phenyldiazonium chloride with 9 different *CH*-active compounds afforded corresponding formazan only in the case of phenylpyruvic acid. Reaction in malonamide gave 3-carbamoyl-1,5-diphenylformazan instead of the expected 1,5-diphenylformazan.

Useful synthetic methods for the preparation of formazans, as reviewed by Nineham almost 40 years ago,[1] are of two types. The first comprises variations of the azo-coupling of diazonium salts with aldehyde arylhydrazones in strongly basic media. It allows access to both symmetrically and unsymmetrically *N,N'*-disubstituted formazans, and is the only general method for 1,3,5-triarylformazans. With some exceptions,[1,2] most yields are poor to moderate and isolation is tedious. The toxicity of the pyridine solvent used seriously limits scale up.

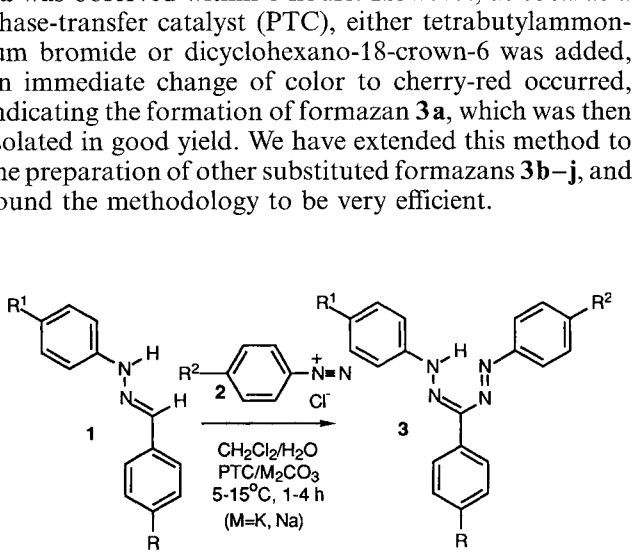
The second type based on the coupling of diazonium salts with active methylene or methine compounds leads only to symmetrically *N,N'*-disubstituted formazans. Yields depend strongly on the type of substituents at the active methylene group (nitro, carboxy, or carboxy derivatives are often employed). The final products are either arylhydrazones or formazans if one of the substituents at the reaction center of the hydrazone formed is expelled by a second molecule of the diazonium compound.[3] The basicity of the medium, ratio of reagents, and type of the substituents play a key role in this reaction: in some cases, different 3-substituted 1,5-diarylformazans could be obtained from the same compound with an active methylene group.[4,5] Moreover, the substituents at the carbon atom are limited (with few exceptions) to non-aromatic structures.

The disadvantages of diazonium salts, such as instability and insolubility in low-polar media, have recently promoted an intensive study of phase-transfer-catalyzed reactions utilizing diazonium salts. The reactions investigated were mostly accompanied by solid-liquid phase-transfer catalysis.[6–9] Subsequently, Hashida et al. found that azo-coupling of arenediazonium salts with compounds having either an activated methylene group or an activated position in an arene moiety occurs readily in liquid-liquid systems and is significantly accelerated by tetraalkylammonium salts.[10] Yields of azo compounds obtained varied from 40 to 90% when a tetraalkylammonium salt was employed as a phase-transfer catalyst in water/1,2-dichloroethane systems.

We now wish to report the preparation of formazans in two-phase (liquid-liquid) media catalyzed by either tetraalkylammonium salts or dicyclohexano-18-crown-6 starting both from arylaldehyde arylhydrazones and from compounds containing an activated methylene group.

1. Reaction of Diazonium Salts With Arylaldehyde Arylhydrazones

When a solution of phenyldiazonium chloride **2a** (R^2 = H, Scheme 1) in water is added to a vigorously stirred mixture containing a solution of benzaldehyde phenylhydrazone **1a** (R = R^1 = H) in dichloromethane and a solution of mild base (sodium or potassium carbonate) in water, no appreciable formation of formazan **3a** was observed within 6 hours. However, as soon as a phase-transfer catalyst (PTC), either tetrabutylammonium bromide or dicyclohexano-18-crown-6 was added, an immediate change of color to cherry-red occurred, indicating the formation of formazan **3a**, which was then isolated in good yield. We have extended this method to the preparation of other substituted formazans **3b–j**, and found the methodology to be very efficient.

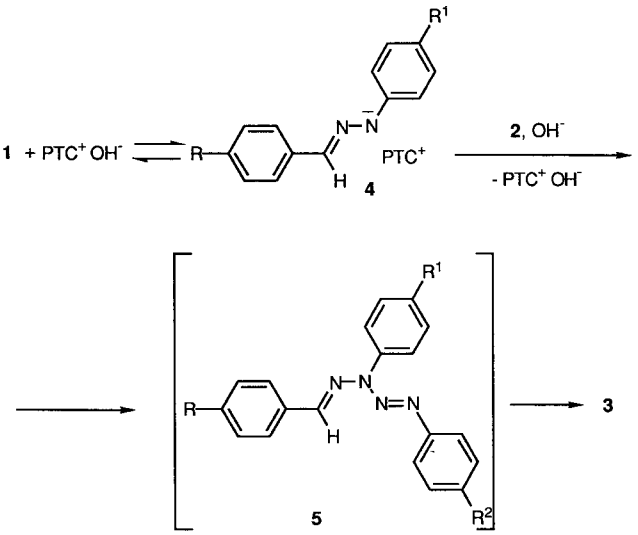


1, 2, 3:	a	b	c	d	e	f	g	h	i	j
R:	H	MeO	Me	NHAc	F	Cl	Ph	NO_2	H	MeO
R^1:	H	H	H	H	H	H	H	H	NO_2	H
R^2:	H	H	H	H	H	H	H	H	H	NO_2

Scheme 1

A possible mechanism, based on the theory of phase-transfer catalysts[11,12] which assumes that interaction proceeds in the water phase, is outlined in Scheme 2. Busch et al.[13,14] postulated that tetrazene **5** is formed first and displacement of hydrogen at the *C*-atom to give formazan **3** follows, because when the *N*-hydrogen atom in the molecule of hydrazone **1** was replaced by a methyl or benzyl group, no formazan was obtained. However, in their detailed study of guanazyl preparation, Scott et al.[15] postulated that azo-coupling proceeds directly at the *C*-atom of hydrazone **1**. In our case, anion formation

under the action of a mild base (sodium or potassium carbonate) will occur at the more acidic *NH* rather than at the *CH* of hydrazone **1**; the ambident anion thus formed could either azo-couple at the nitrogen atom with subsequent rearrangement of the unstable tetrazene **5** into formazan **3**, or give **3** directly.



Scheme 2

Table 1. Preparation of 1,3,5-Triarylformazans[a]

3	Yield (%)[b] (Lit. yield)	mp (°C) found	mp (°C) reported	Catalyst[c]	Reaction Time (h)	Method of Isolation[d]
a	71 (44[4])	172–174	176[4]	TBABr	1	A
a	55	174–175		TBABs	1	A
a	61	171–173		DC18C6/ K_2CO_3	2	A
b	53 (30[16])	157–159	156–158[16]	TBABr	2	B
c	54	166–168	170[17]	TBABr	2	B
d	42 (53[2])	210–211	206–207[2]	TBABr	4	C
e[e]	63	194–195		TBABr	1	D
f	60	195–196	190[18]	TBABr	1	D
g	48 (44[19])	193–194	194–195[19]	TBABr	4	C
h	51 (40[2])	204–205	204[2]	TBABr	2	D
i	45	165–167	165–170[2]	TBABr	1	C
j	77 (70[20])	181–182	182–183[20]	TBABr	2	D

[a] Conditions: ratio **1** : **2** : base = 1 : 1.1 : 5; catalyst: 10% mol; temperature: 5–15°C; base: Na_2CO_3 (except where specified).

[b] Yields of pure formazans.

[c] TBABr: tetrabutylammonium bromide; TBABs: tetrabutylammonium hydrogen sulfate; DC18C6: dicyclohexano-18-crown-6.

[d] A: trituration with methanol; B: recrystallization from benzene; C: recrystallization from aqueous DMF; D: recrystallization from aqueous dioxane.

[e] ^1H NMR ($CDCl_3$/TMS): δ = 8.08 (dd, 2H, J = 5, 9.5 Hz), 7.65 (d, 4H, J = 7.5 Hz), 7.45 (t, 4H, J = 7.5 Hz), 7.28 (t, 2H, J = 7.5 Hz), 7.11 (t, 2H, J = 7.5 Hz).
^{13}C NMR ($CDCl_3$/TMS): δ = 147.7, 140.4, 134.6, 129.4, 127.5, 118.7, 115.3, 115.0, 111.2.
$C_{19}H_{15}FN_4$ (318.4) calc. C 71.67 H 4.75 N 17.60 found 71.50 4.69 17.58

The experimental data are collected in Table 1. As shown for **3a**, onium salts have demonstrated better catalytic activity than dicyclohexano-18-crown-6. Of the two tetrabutylammonium salts studied, the bromide was more effective than the hydrogen sulfate. Yields of the crude formazans **3b–j** were higher than 80%; often simple trituration of the crude formazan (isolated from the organic layer by the traditional workup procedure) with methanol followed by filtration gave the pure formazan **3**; some required an additional recrystallization to obtain analytically pure samples. The method works smoothly for both electron-donating and electron-withdrawing substituents. Even hydrazones **1d,g** with limited solubility in dichloromethane gave reasonably good yields of formazans provided the reaction time was extended to 4 hours. Similarly, an extended reaction time was necessary for the less reactive hydrazones **1b,c**. However, TLC data indicated that hydrazone **1** is consumed during the first hour of reaction. A reduced excess of the diazonium component compared with the traditional method decreases the likelihood of side reactions.

Three important experimental details should be noted: first, the reaction proceeds at temperatures which are higher than normally required for azo-coupling; second, the reaction is not as exothermic as in the case of azo-coupling in pyridine; third, the basicity of the aqueous phase is lower than in the traditional pyridine synthesis.

2. Reactions of Aryldiazonium Salts With Compounds Containing an Active Methylene Group

More complicated results were obtained when such reactions were carried out under PTC conditions. As already mentioned, even traditional azo-coupling of diazonium salts with *CH*-active compounds depends on a variety of factors. We attempted the syntheses of formazans from different *CH*-active compounds and phenyldiazonium chloride under various PTC conditions. The results of this study are summarized in Table 2.

Azo-coupling in each case was monitored by comparison of the TLC of the crude reaction products with the TLC of formazans prepared by known methods: 3-cyano-1,5-diphenylformazan (entries 1–4),[5] 3-ethoxycarbonyl-1,5-diphenylformazan (entry 5),[21] 1,5-diphenylformazan (entries 6, 7),[5] and 1,3,5-triphenylformazan (entries 8, 9).[22]

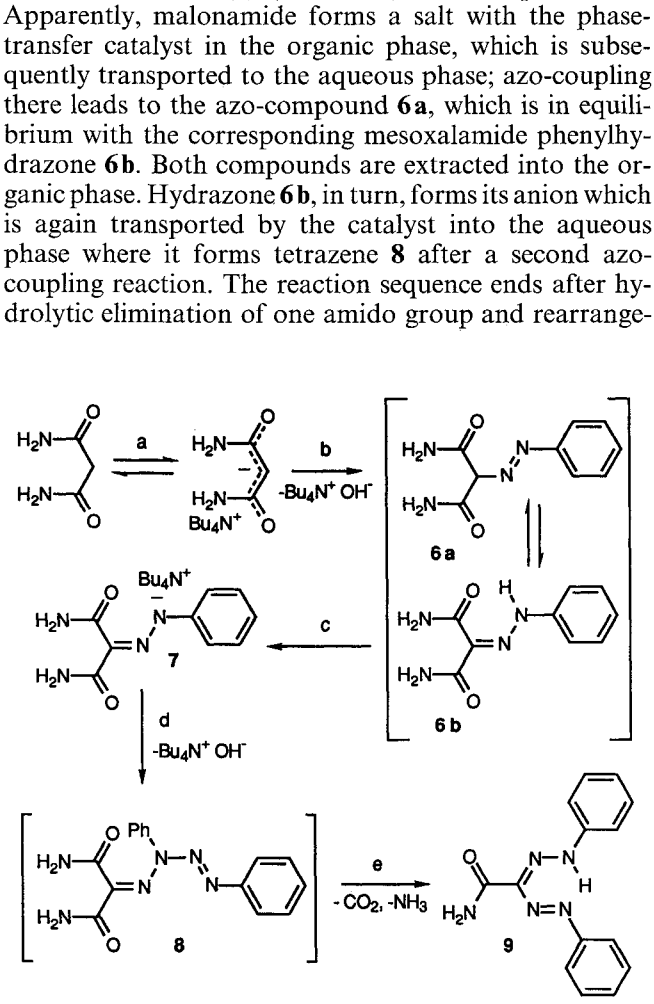
No formazan was formed from cyanoacetic ester (entries 1–3), irrespective of the pH and catalyst used; a complicated mixture of products was obtained in each trial. A small amount of 3-cyano-1,5-diphenylformazan was detected when cyanoacetic acid was coupled with phenyldiazonium chloride at pH 12–13 (entry 4). Neither acetoacetic ester (entry 5), nor malonic ester (entry 6) reacted with phenyldiazonium chloride under the conditions used to give the expected 3-ethoxycarbonyl-1,5-diphenylformazan and 1,5-diphenylformazan. Malonamide (entry 7) gave a surprising result. According to literature data,[5] azo-coupling of malonamide with aryldiazonium salts leads to 1,5-diarylformazans at pH 13–14, and to 1,5-diaryl-3-carbamoylformazans at pH 9–10; obviously, the formation of 1,5-diarylformazans

Table 2. Azo-Coupling of *CH*-Active Compounds with Phenyldiazonium Chloride[a]

Entry	*CH*-Active Compound	Base	Catalyst[b]	pH	Results of Azo-Coupling	
					Formazan	Other Products
1	$NCCH_2CO_2Et$	–	–	4–5[c]	–	+
2	$NCCH_2CO_2Et$	Na_2CO_3	TBABr	7–8	–	+
3	$NCCH_2CO_2Et$	NaOH (10%)	TBABs	9–10	–	+
4	$NCCH_2CO_2H$	NaOH (25%)	TBABs	12–13	+	+
5	$MeCOCH_2CO_2Et$	NaOH (10%)	TBABs	9–10	–	+
6	$EtO_2CCH_2CO_2Et$	NaOH (10%)	TBABs	9–10	–	+
7	$H_2NOCCH_2CONH_2$	NaOH (25%)	TBABs	12–13	+	+
8	$PhCH(CO_2H)_2$	NaOH (25%)	TBABs	12–13	–	+
9	$PhCH_2COCO_2H$	NaOH (25%)	TBABs	12–13	+	–

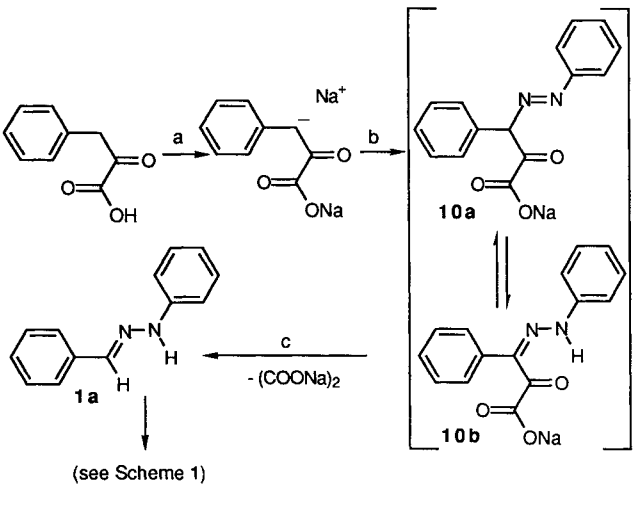
[a] Conditions: ratio diazonium salt : substrate : base = 2.2 : 1 : 10; media: CH_2Cl_2/water (entries 1–4, 9), toluene/water (entries 5–8); temperature: 0–5 °C; reaction time: 3 h; catalyst: 10% mol.
[b] For abbreviations, see Table 1.
[c] Buffered media; pH 4–5 was used according to literature.[3]

is a stepwise elimination ("hydrolytic removal"[5]) of both carbamoyl groups in strongly basic media. However, in our case the only product isolated was 3-carbamoyl-1,5-diphenylformazan (**9**) (Scheme 3), even at pH 12–13. Apparently, malonamide forms a salt with the phase-transfer catalyst in the organic phase, which is subsequently transported to the aqueous phase; azo-coupling there leads to the azo-compound **6a**, which is in equilibrium with the corresponding mesoxalamide phenylhydrazone **6b**. Both compounds are extracted into the organic phase. Hydrazone **6b**, in turn, forms its anion which is again transported by the catalyst into the aqueous phase where it forms tetrazene **8** after a second azo-coupling reaction. The reaction sequence ends after hydrolytic elimination of one amido group and rearrangement of the tetrazene into formazan **9**. Hydrolytic elimination of the second carbamoyl group does not occur, probably because of the absence of water in the organic phase.



(a) $Bu_4N^+OH^-$, toluene/H_2O; (b) phenyldiazonium chloride; (c) $Bu_4N^+OH^-$; (d) phenyldiazonium chloride; (e) H_2O

Scheme 3



(a) NaOH; (b) phenyldiazonium chloride/NaOH; (c) H_2O/NaOH

Scheme 4

1,3,5-Triphenylformazan (**3a**) was not obtained in the case of phenylmalonic acid (entry 8). However, β-phenylpyruvic acid smoothly gave **3a** in 57% yield (entry 9). As shown in Scheme 4, the first azo-coupling results in the formation of azo-compound **10a** and related hydrazone **10b**, which is hydrolysed into hydrazone **1a**. Subsequent extraction of **1a** into the organic phase initiates the further sequence of transformations depicted in Scheme 1.

The differing reactivity of compounds with active methylene groups may be explained as follows. In the case of acetic acid ester derivatives (entries 1–3, 5, 6), the hydrazone formed from the first coupling reaction is extracted into the organic phase, and thus excluded from

the reaction site. Cyanoacetic acid (entry 4) gives the corresponding formazan, only in negligible yield probably because of the inhibiting action of the onium cation on the decarboxylation process, a key step in the preparation of formazans from carboxylic acids and their derivatives.[1] In the case of the diacid (entry 8) this effect is even more pronounced, i.e., no formazan was formed. Two other entries, 7 and 9, led to successful formazan preparations, as discussed above.

3. One-Pot Synthesis of 1,3,5-Triarylformazans.

A one-pot procedure for 1,3,5-triphenylformazan preparation, proposed by Mattson et al.,[22] includes condensation of benzaldehyde with phenylhydrazine in methanol, addition of the resultant mixture to a methanol solution of sodium hydroxide/sodium acetate followed by addition of phenyldiazonium chloride at 20 °C. The yield of formazan **3a** using this procedure was only 23%.

An example of the direct syntheses of triarylformazans by azo-coupling of malonic acid with an excess of aryldiazonium chlorides in dimethylformamide/pyridine mixture was described by Neugebauer and Küchler.[4] 1,5-Diarylformazans, formed during azo-coupling with two molecules of aryldiazonium salt, were then coupled with a third molecule to give 3-arylazo-1,5-diarylformazans. Loss of molecular nitrogen afforded the target 1,3,5-triarylformazans in 8–44% yields. However, this method is restricted only to the formazans with identical aryl substituents at the *C,N,N*-atoms of the formazan system.

The reaction of arylaldehydes with arylhydrazines is well-known and usually gives high yields of arylhydrazones under acidic catalysis. We demonstrated using the example of formazan **3a**, that its preparation could be successfully achieved in a one-pot procedure starting from benzaldehyde and phenylhydrazine. Indeed, condensation of these two reagents in toluene in the presence of catalytic amounts of *p*-toluenesulfonic acid, followed by phase-transfer catalyzed azo-coupling procedure as per hydrazone **1a** (Scheme 1), afforded 1,3,5-triphenylformazan in 54% yield. This method allows the omission of the arylaldehyde arylhydrazone isolation and renders this formazan synthesis straightforward.

In conclusion, the proposed phase-transfer catalyzed azo-coupling of aryldiazonium salts with either arylhydrazones of arylaldehydes or with compounds containing active methylene groups makes the preparation of formazans more efficient and simple. This method encompasses all of the advantages of traditional phase-transfer catalysis, e.g., selectivity, ease of workup procedure, rapidity, and can be successfully extended to the preparation of a variety of substituted formazans.

Melting points were measured with a Kofler Hot Stage apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra of 3-(4-fluorophenyl)-1,5-diphenylformazan (**3e**) were recorded on a Varian Gemini-300 spectrometer; chemical shifts are reported in ppm (δ) downfield from TMS as an internal standard. Thin-layer chromatography was monitored using Kodak Chromatogram Sheets (silica gel) with $CHCl_3$ as an eluent.

Starting compounds and solvents were commercially available (Aldrich, Fisher, Eastman-Kodak, and Sigma) and were used as received. Arylhydrazones of arylaldehydes were prepared as described in the literature.[23] 1,5-Diphenylformazan, 3-cyano-1,5-diphenylformazan, 3-ethoxycarbonyl-1,5-diphenylformazan, and 1,3,5-triphenylformazan as reference compounds for thin-layer chromatography were prepared as previously described.[5,21,22]

1,3,5-Triarylformazans 3a–j; Typical Procedures:

1,3,5-Triphenylformazan (**3a**) Method A:

A mixture of benzaldehyde phenylhydrazone (**1a**; 0.98 g, 5 mmol) $Na_2CO_3 \cdot H_2O$ (3.10 g, 25 mmol), Bu_4NBr (0.16 g, 0.5 mmol), CH_2Cl_2 (50 mL), and H_2O (20 mL) was vigorously stirred for 10 min, followed by dropwise addition at 5 °C of a solution of diazonium salt prepared according to the literature procedure[23] from aniline (0.52 mL, 5.75 mmol), conc. HCl (1.3 mL), and $NaNO_2$ (0.47 g, 6.85 mmol) in H_2O (total volume 30 mL). After stirring for 1 h (during this time the mixture was allowed to warm to r.t.), the organic layer was separated, washed with water (2 × 50 mL), separated, and dried (Na_2SO_4). Evaporation of the solvent in vacuo gave crude product, which was recrystallized from aq dioxane to give 1.06 g (71%) of deep-red prisms of **3a** (Table 1).

1,3,5-Triphenylformazan (**3a**) Method B:

Method B involves the same procedure as given in Method A, except that K_2CO_3 (3.45 g, 25 mmol) and dicyclohexano-18-crown-6 (0.093 g, 0.25 mmol) were used as the base and phase-transfer catalyst, respectively. Pure **3a** in the form of red prisms was isolated in a yield of 0.92 g (61%) after recrystallization from aq dioxane (see Table 1).

1,3,5-Triphenylformazan (**3a**) Method C:

A mixture of phenylpyruvic acid sodium salt monohydrate (1.02 g, 5 mmol), NaOH (20 mL of 10% w/w aq solution, 25 mmol), Bu_4NHSO_4 (0.17 g, 0.5 mmol), CH_2Cl_2 (40 mL), and H_2O (20 mL) was vigorously stirred for 15 min followed by dropwise addition at 5 °C of a solution of diazonium salt prepared according to the known literature procedure[23] from aniline (1.00 mL, 11 mmol), conc. HCl (2.85 mL), and $NaNO_2$ (0.95 g, 13.7 mmol) in H_2O (total volume 30 mL). After stirring for 1 h (during this time the mixture was allowed to warm to r.t.), the organic layer was treated as described for Method A. Flash column chromatography of the dried organic layer on silica gel (eluent CH_2Cl_2) afforded the first ruby red fraction which after evaporation of the solvent and trituration of the crystalline residue with MeOH (10 mL), followed by filtration, gave 0.85 g (57%) of **3a** as red microcrystals; mp 169–171 °C.

1,3,5-Triphenylformazan (**3a**) Method D; *One-Pot Procedure:*

A mixture of benzaldehyde (0.51 mL, 5 mmol), phenylhydrazine (0.49 mL, 5 mmol), and TsOH (20 mg) in toluene (50 mL) was heated at 70 °C for 15 min with stirring. The solution was then cooled to 0 °C, and $Na_2CO_3 \cdot H_2O$ (3.10 g, 25 mmol), Bu_4NBr (0.16 g, 0.5 mmol), and H_2O (20 mL) were added. The mixture was vigorously stirred for 10 min, followed by dropwise addition of a solution of diazonium salt prepared from aniline (0.52 mL, 5.75 mmol) as described in Method A. After stirring for 2 h, the toluene layer was worked up as described in Method A. Evaporation of the solvent, recrystallization of the crude formazan from aq DMF, and filtration gave 0.81 g (54%) of red prisms of **3a**; mp 173–174 °C.

1,3,5-Triarylformazans **3b–j** were prepared from the corresponding arylaldehyde arylhydrazones according to Method A.

3-Carbamoyl-1,5-diphenylformazan (9):

A mixture of malonamide (0.510 g, 5 mmol), NaOH (2.00 g, 50 mmol), Bu_4NHSO_4 (0.17 g, 0.5 mmol), toluene (30 mL), and H_2O (10 mL) was stirred at 5 °C for 5 min. A diazonium salt solution prepared from aniline (1.00 mL, 11 mmol) as described above for compound **3a** (Method C) was added dropwise at 5–10 °C over 0.5 h, followed by continued stirring for an additional 0.5 h. Partially precipitated formazan was filtered, and the filtrate was worked up as described above for compound **3a** (Method A). Evaporation of the organic solvent gave crude formazan which was combined with the previously filtered portion, triturated with MeOH (10 mL), and filtered to give 0.51 g (38%) of formazan **9** in the form of brick-red needles; mp 194–195 °C (lit.[5] mp 195–196 °C).

The attempted syntheses of formazans from compounds containing an active methylene group were carried out according to the procedure for the preparation of formazan **9** using a variety of solvents and reaction times (Table 2).

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