1-Arylideneamino-2,2,2-trichloroethanols as synthetic equivalents of arylideneimines in the reaction with cyclopropenone derivatives

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1-Arylideneamino-2,2,2-trichloroethanols react regiospecifically with cyclopropenones to form 2,2′-diaryl-1,1′,2,2′-tetrahydro-3*H*,3′*H*-2,2′-bipyrrole-3,3′-diones. A new preparative method was developed for the synthesis of 1-arylideneamino-2,2,2-trichloroethanols.

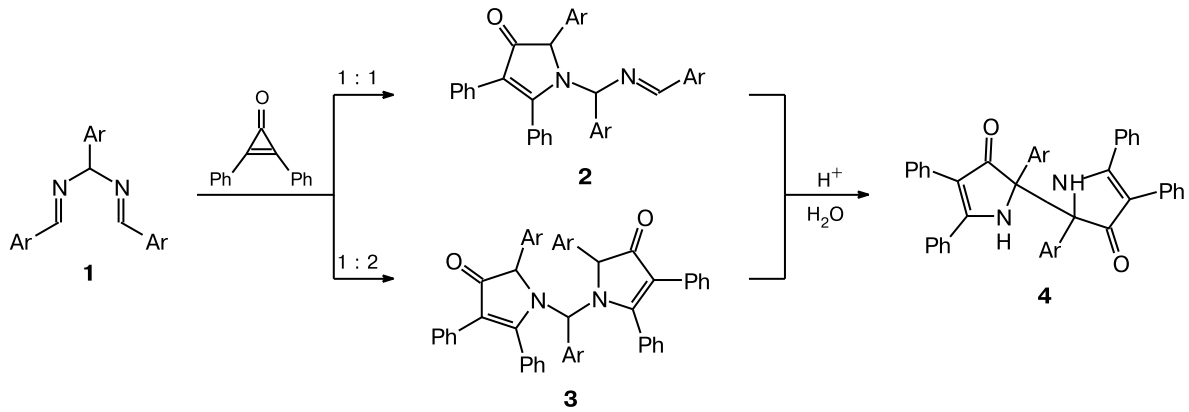
Key words: 1-arylideneamino-2,2,2-trichloroethanols, dihydropyrrolones, cyclopropenones, oxidative dimerization.

A general strategy of our studies is the search for physiologically active compounds containing two covalently bonded pharmacophoric groups in the molecule ("twin-drugs"), in particular, for their synthesis from easily available bis(imines), *viz.*, 1-aryl-*N*,*N*′-bis(arylidene)methanediamines **1** (see Ref. 1). We have earlier shown[2] that bis(imines) **1** can be used as synthetic equivalents of *N*-unsubstituted arylideneimines in the reaction with cyclopropenones (Scheme 1). The process is regioselective and allows one to synthesize both dihydropyrrolones **2** and bis(1,2-dihydropyrrolonyl)methanes **3** that form substituted 2,2′-bis(dihydropyrrolones) **4** upon hydrolysis and subsequent oxidative dimerization of intermediate 2-aryl-4,5-diphenylhydropyrrol-3-ones (see Scheme 1).

At the same time, this reaction is not universal: the starting compounds containing aryl groups with electron-withdrawing substituents are poorly available.[3] In addition total yields of bis(pyrrolones) **4** in two steps do not exceed 40%. In this work we continued to search for potent synthetic equivalents of arylideneimines. We assumed that 1-arylideneamino-2,2,2-trichloroethanols **5**, which have first been prepared by Schiff[4] in 1877, can be used for our purpose. The synthesis of the latter were repeatedly described[5] in 1948 as a one-step process from cheap chloral hydrate, ammonia, and benzaldehyde (Scheme 2).

However, we have confirmed many times that the only product formed under the described conditions is the adduct of ammonia and benzaldehyde, $PhCH(N{=}CHPh)_2$ (**1a**). The further study of the process made it possible to modify it, and we showed that 1-arylideneamino-2,2,2-trichloroethanols **5** can be obtained by the exothermic reaction in yields from 50 to 85% by passing dry ammonia through a solution of aromatic aldehyde and chloral excess

Scheme 1



Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-MeC_6H_4 (**c**)

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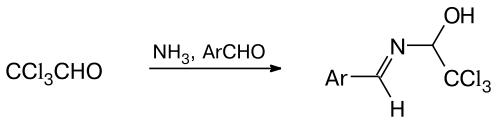
Scheme 2



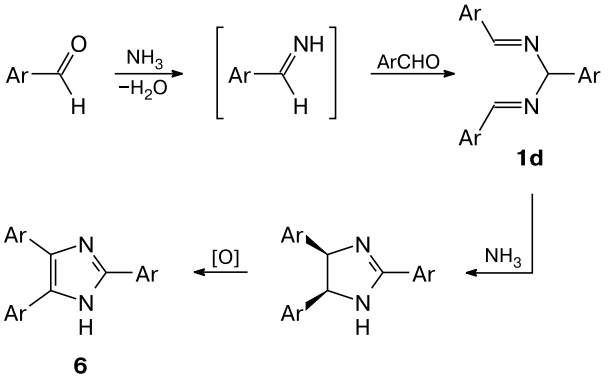
5a—h

Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-MeC_6H_4 (**c**), 4-$O_2NC_6H_4$ (**d**), 2-thienyl (**e**), 3-pyridyl (**f**), 2,6-$Cl_2C_6H_3$ (**g**), 3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl (**h**)

(1.5—2 equiv.) in diethyl ether on cooling to −10 °C (see Scheme 2).

The process can be catalyzed by anhydrous zinc chloride, *p*-toluenesulfonic acid, or ammonium chloride. In the presence of catalyst, the major part of product **5** is formed within several minutes; however, the highest yields are achieved when the reaction is carried out for several hours. The yield does not decrease substantially without a catalyst; however, the reaction is retarded and completed within ~20 h. Aromatic aldehydes with both electron-donating and electron-withdrawing substituents in the aromatic ring can be involved in the process, which makes the transformation rather general. The exception is the reaction with 4-nitrobenzaldehyde forming 2,4,5-tris-(4-nitrophenyl)-1*H*-imidazole (**6**) (Scheme 3). It is likely that the reaction proceeds *via* formation of imine transformed into 1-(4-nitrophenyl)-*N*,*N*-bis(4-nitrobenzylidene)methanediamine (**1d**), which undergoes electrocyclic ring closure to form *cis*-imidazoline. The latter is readily oxidized with air oxygen to the corresponding imidazole **6** (see Scheme 3).

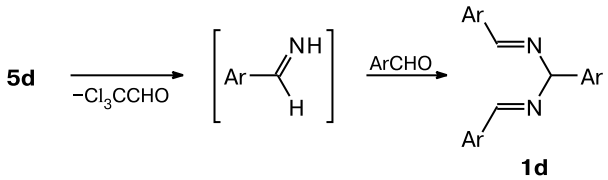
Scheme 3



Ar = 4-$O_2NC_6H_4$

1-Arylideneamino-2,2,2-trichloroethanols **5** with both electron-withdrawing and electron-donating groups were synthesized in 38—95% yields using the modified Schiff procedure.[6] The process was accomplished in two particular steps: the adduct of chloral with ammonia was obtained first, which was, most likely, a mixture of several compounds, with unknown exact composition,[6,7] and then a twofold excess of this adduct was introduced into the reaction with aromatic aldehyde in dichloromethane in the presence of catalytic amounts of *p*-toluenesulfonic acid. This modification of the process makes it possible to obtain nitro derivative **5d**, from which poorly available *N*,*N*-bis(4-nitrobenzylidene)methanediamine **1d** can be synthesized in turn. The latter is formed in 84% yield on heating of compound **5d** in benzene for 8.5 h (Scheme 4). Compound **1d** undergoes ring closure and is oxidized to imidazole **6** by longer heating (18 h) under normal conditions. Since the melting points measured for compounds **1d** and **6** did not coincide with the published values and the literature data for these compounds are contradictory, the formation of the corresponding product was confirmed by elemental analysis in the both cases.

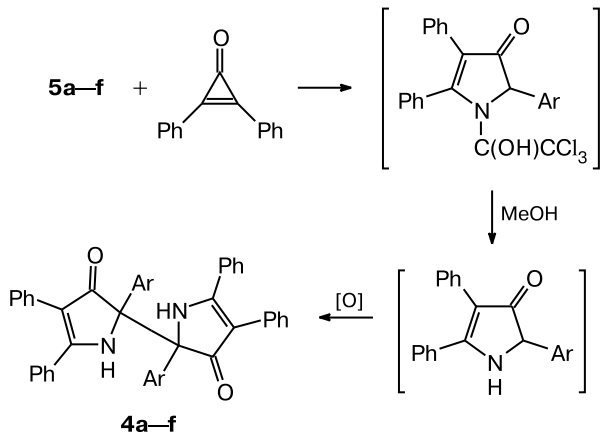
Scheme 4



Ar = 4-$O_2NC_6H_4$

We also showed that 1-arylideneamino-2,2,2-trichloroethanols **5** reacted with diphenylcyclopropenone at room temperature in methanol to form 2,2′-diaryl-4,4′,5,5′-tetraphenyl-1,1′,2,2′-tetrahydro-3*H*,3′*H*-2,2′-bipyrrole-3,3′-diones (**4a—f**) (Scheme 5). In the case of compounds **5g**,**h**, a complicated mixture of non-identified products was formed.

Scheme 5

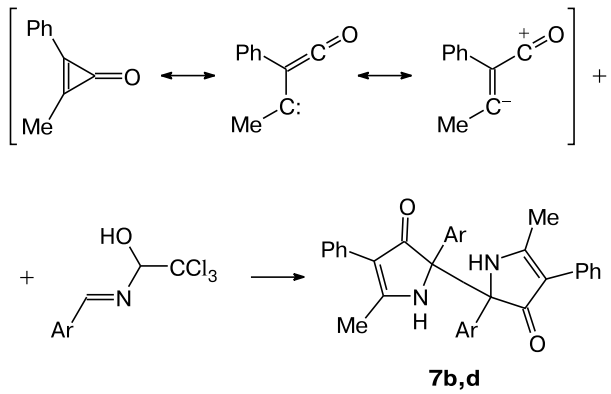


Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-MeC_6H_4 (**c**), 4-$O_2NC_6H_4$ (**d**), 2-thienyl (**e**), 3-pyridyl (**f**)

The removal of the protective group followed by oxidative dimerization occurs during the reaction (see Scheme 5). The intermediate can be assumed to undergo the nucleophilic attack by methanol with the elimination of $Cl_3CCH(OMe)OH$. This compound was detected in the reaction mixture by ^1H NMR spectroscopy (two singlets at δ_H 3.61 and 4.86, integral intensity ratio 3 : 1). Compounds **4a—c** were synthesized and characterized earlier.[2,3]

Nonsymmetric 3-methyl-2-phenylcyclopropenone regiospecifically reacts with 1-arylideneamino-2,2,2-trichloroethanols **5** to form only one isomer **7** (Scheme 6). This fact is due apparently to the greater stability of the intermediate with the phenylketene structure compared to that with the methylketene structure.

Scheme 6



7b,d

Ar = 4-$MeOC_6H_4$ (**b**), 4-$O_2NC_6H_4$ (**d**)

The formation of 5-methyl-4-phenylpyrrolone **7** rather than its regioisomer was proved for product **7b** (Ar = = 4-$MeOC_6H_4$) by ^1H NMR spectroscopy using the nuclear Overhauser effect. Additional irradiation was carried out at the proton frequency δ_H 9.37 (NH moiety), which induced proton responses at δ_H 2.11 (CH_3, 7.5%) and 7.82 (H_{Ar} in the *meta*-position to the MeO group, 6.3%), and no response on the *ortho*-protons of the phenyl group (δ_H 6.91) was observed.

The dimeric structure of compounds **7** is indicated by the absence of a signal of the proton in position 2 of the pyrrole ring in the ^1H NMR spectra (for **7b**) and the presence of peaks corresponding to decomposition with 1,5-migration of the hydrogen atom in the mass spectrum (*m/z* 279, 277 for **7b** and *m/z* 294, 292 for **7d**), as well as the elemental analysis data (in the corresponding monomeric products the hydrogen content would be higher).

This method of synthesis of 2,2′-diaryl-4,4′,5,5′-tetraphenyl-1,1′,2,2′-tetrahydro-3*H*,3′*H*-2,2′-bipyrrole-3,3′-diones **4** have several advantages over both the earlier proposed method[2] and the synthesis of the latter from azines[8]: the process is one-step, occurs without losses of aromatic aldehyde, and makes it possible to extend the scope of aromatic aldehydes, including heteroaromatic aldehydes and aldehydes containing electron-withdrawing groups.

Experimental

^1H NMR spectra were recorded on a Bruker Avance-400 instrument with a working frequency of 400.13 MHz for ^1H and 100.61 NHz for ^{13}C. IR spectra were measured on a Carl Zeiss UR-20 spectrophotometer in Nujol. Elemental analysis was carried out on a Carlo Erba automated analyzer. Melting points were measured using an Electrothermal 9100 melting point indicator in a sealed capillary and uncorrected. Mass spectrometric analyses were carried out on a Finnigan MATINCOSSO mass spectrometer (EI, 70 eV, direct inlet).

1-Arylideneamino-2,2,2-trichloroethanols 5a—h (general procedure). ***A.*** Dry ammonia was passed through a solution of chloral, aromatic aldehyde, and catalytic amounts of *p*-toluenesulfonic acid in dry diethyl ether cooled to −20—−15 °C with vigorous stirring maintaining the reaction temperature below 0 °C, after which stirring continued at room temperature. The precipitate formed was collected by filtration, and an additional portion of the product was isolated from the mother liquor after evaporation of the solvent and washing of the residue with a small amount of diethyl ether. An analytically pure sample was obtained by recrystallization from benzene.

B. Dry ammonia was passed through a solution of chloral (19.6 g, 0.133 mol) in anhydrous chloroform (30 mL) with vigorous stirring at temperatures from −5 to −10 °C until the reaction mixture solidified. A colorless amorphous product (13.2 g) was separated by filtration and washed with diethyl ether. The obtained material was dissolved in anhydrous dichloromethane and aromatic aldehyde and catalytic amount of *p*-toluenesulfonic acid were added. The reaction mixture was stirred at room temperature. The precipitate formed was separated by filtration. An analytically pure sample was obtained by recrystallization from benzene.

1-[(*E*)-Benzylideneamino]-2,2,2-trichloroethanol (5a). Compound **5a** was synthesized by method ***A*** from chloral (1.66 g, 11.3 mmol) and benzaldehyde (1.8 g, 9.9 mmol) in anhydrous diethyl ether (5 mL) within 18 h in a yield of 1.21 g (48%), colorless crystals, m.p. 131—132 °C (benzene) (*cf.* Refs 6 and 7: m.p. 130 °C (benzene)). ^1H NMR ($CDCl_3$), δ: 3.75 (br.s, 1 H, OH); 5.21 (s, 1 H, O—CH—N=); 7.46—7.55 (m, 3 H, H_{Ar}); 7.86 (d, 2 H, H_{Ar}, J = 7.4 Hz); 8.59 (s, 1 H, CH=N). ^{13}C NMR (DMSO-d_6), δ: 93.61 (O—CH—N); 102.64 (quatern., CCl_3); 129.59; 132.20; 132.35; 134.25 (quatern.); 159.58 (C=N). IR, ν/cm^{-1}: 1580; 1605; 1640 (C=N); 2600—3400 (bonded, OH).

Compound **5a** was synthesized by method ***B*** from the adduct of chloral with ammonia (5.08 g) and benzaldehyde (2.10 g, 19.8 mmol) in anhydrous dichloromethane (3 mL) within 15 h in a yield of 2.78 g (56%).

1-[(*E*)-(4-Methoxybenzylidene)amino]-2,2,2-trichloroethanol (5b). Compound **5b** was synthesized by method ***A*** from chloral (8.46 g, 57.9 mmol) and 4-methoxybenzaldehyde (4.48 g, 33.2 mmol) in anhydrous diethyl ether (10 mL) within 23 h in a yield of 6.64 g (72%); colorless crystals, m.p. 140—141 °C (*cf.* Ref. 7: m.p. 141—142 °C (benzene)). ^1H NMR ($CDCl_3$), δ: 3.87 (s, 3 H, OCH_3); 4.17 (br.s, 1 H, OH); 5.15 (s, 1 H, O—CH—N=); 6.96 (d, 2 H, H_{Ar}, J = 8.6 Hz); 7.81 (d, 2 H, H_{Ar},

J = 8.6 Hz); 8.49 (s, 1 H, CH=N). ^{13}C NMR (DMSO-d_6), δ: 55.86 (CH_3O); 94.82 (N—CH—O); 103.72 (quatern., CCl_3); 114.71; 128.45 (quatern.); 130.99; 162.55 (quatern.); 163.13 (C=N). IR, ν/cm^{-1}: 1610; 1640 (C=N); 2800—3280 (bonded, OH).

Compound **5b** was synthesized by method ***B*** from the adduct of chloral with ammonia (2.75 g) and 4-methoxybenzaldehyde (1.12 g, 8.3 mmol) in anhydrous dichloromethane (3 mL) within 23 h in a yield of 2.04 g (88%).

1-[(*E*)-(4-Methylbenzylidene)amino]-2,2,2-trichloroethanol (5c). Compound **5c** was synthesized by method ***A*** from chloral (2.43 g, 16.4 mmol) and 4-methylbenzaldehyde (1.8 g, 15.0 mmol) in anhydrous diethyl ether (5 mL) within 2 h in a yield of 2.57 g (64%); colorless crystals, m.p. 143—144 °C (*cf.* Ref. 5: m.p. 144—145 °C (benzene)). ^{1}H NMR ($CDCl_3$), δ: 2.40 (s, 3 H, CH_3); 5.10 (br.s, 1 H, OH); 5.25 (s, 1 H, O—CH—N=); 7.24 (d, 2 H, H_{Ar}, J = 7.8 Hz); 7.73 (d, 2 H, H_{Ar}, J = 7.8 Hz); 8.55 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$—DMSO-d_6), δ: 21.47 (CH_3); 95.05 (N—CH—O); 102.74 (quatern., CCl_3); 128.92; 129.26; 132.62 (quatern.); 142.01 (quatern.); 163.44 (C=N). IR, ν/cm^{-1}: 1580; 1610; 1640 (C=N); 2800—3300 (bonded, OH).

1-[(*E*)-(4-Nitrobenzylidene)amino]-2,2,2-trichloroethanol (5d). Compound **5d** was synthesized by method ***B*** from the adduct of chloral with ammonia (6.51 g) and 4-nitrobenzaldehyde (3.0 g, 19.9 mmol) in anhydrous dichloromethane (16 mL) within 2 h in a yield of 4.0 g (68%); light yellow crystals, m.p. 124—127 °C (*cf.* Ref. 5: m.p. 123.5—124 °C (benzene)). ^{1}H NMR ($CDCl_3$), δ: 3.85 (br.s, 1 H, OH); 5.41 (s, 1 H, O—CH—N=); 8.04 (d, 2 H, H_{Ar}, J = 8.6 Hz); 8.32 (d, 2 H, H_{Ar}, J = 8.6 Hz); 8.72 (s, 1 H, CH=N). ^{13}C NMR (DMSO-d_6—$CDCl_3$), δ: 93.18 (O—CH—N); 102.06 (quatern., CCl_3); 123.48; 129.44; 140.59 (quatern.); 149.00 (quatern.); 160.36 (C=N). IR, ν/cm^{-1}: 1350 (symm., NO_2); 1525 (asymm., NO_2); 1600; 1645 (C=N); 2800—3300 (bonded, OH).

An attempt to prepare compound **5d** by method ***A*** gave 2,4,5-tris(4-nitrophenyl)-4*H*-imidazole (**6**) (see below).

1-[(Thiophen-2-yl)methylideneamino]-2,2,2-trichloroethanol (5e) was synthesized by method ***A*** from chloral (7.87 g, 53.9 mmol) and 2-thiophenecarboxaldehyde (3.03 g, 27.0 mmol) in anhydrous diethyl ether (10 mL) within 21 h in a yield of 3.37 g (48%); colorless crystals, m.p. 139—140.5 °C. Found (%): C, 32.53; H, 2.25; N, 5.35. $C_7H_6Cl_3NOS$. Calculated (%): C, 32.52; H, 2.34; N, 5.42. ^{1}H NMR (DMSO-d_6), δ: 5.28 (s, 1 H, O—CH—N=); 7.06 (dd, 1 H, H_{Ar}, J = 5.1 Hz, J = 3.5 Hz); 7.32 (br.s, 1 H, OH); 7.44 (d, 1 H, H_{Ar}, J = 3.5 Hz); 7.49 (d, 1 H, H_{Ar}, J = 4.8 Hz); 8.67 (s, 1 H, CH=N). ^{13}C NMR (DMSO-d_6), δ: 99.89 (N—CH—O); 103.39 (quatern., CCl_3); 128.60; 131.84; 134.37; 141.78 (quatern.); 157.14 (C=N). IR, ν/cm^{-1}: 1630 (C=N); 2600—3280 (bonded, OH).

Compound **5e** was synthesized by method ***B*** from the adduct of chloral with ammonia (30 g) and 2-thiophenecarboxaldehyde (8.52 g, 76.1 mmol) in anhydrous dichloromethane (22 mL) within 45 h in a yield of 17.8 g (90%).

1-[(Pyridin-3-yl)methylideneamino]-2,2,2-trichloroethanol (5f) was synthesized by method ***B*** from the adduct of chloral with ammonia (4.09 g) and 3-pyridinecarboxaldehyde (1.71 g, 16.0 mmol) in anhydrous dichloromethane (3 mL) within 16 h in a yield of 3.83 g (95%); colorless crystals, m.p. 120—122.5 °C. Found (%): C, 38.07; H, 2.89; N, 11.11. $C_8H_7Cl_3N_2O$. Calculated (%): C, 37.90; H, 2.78; N, 11.05. ^{1}H NMR (DMSO-d_6—$CDCl_3$), δ: 5.41 (s, 1 H, O—CH—N=); 7.32 (dd, 1 H, H_{Ar}, J = 7.6 Hz, J = 4.8 Hz); 8.14 (dt, 1 H, H_{Ar}, J = 7.8 Hz, J = 1.8 Hz); 8.60 (dd, 1 H, H_{Ar}, J = 4.8 Hz, J = 1.8 Hz); 8.64 (d, 1 H, H_{Ar}, J = 1.8 Hz); 8.89 (s, 1 H, CH=N). ^{13}C NMR (DMSO-d_6), δ: 93.86 (O—CH—N); 103.20 (quatern., CCl_3); 124.58; 131.17 (quatern.); 135.62; 150.82; 152.78; 161.30 (C=N). IR, ν/cm^{-1}: 1600; 1645 (C=N); 2400—3250 (bonded, OH).

Compound **5f** was synthesized by method ***A*** from chloral (3.93 g, 26.7 mmol) and 3-pyridinecarboxaldehyde (2.85 g, 26.6 mmol) in anhydrous diethyl ether (10 mL) within 15 h in a yield of 5.72 g (85%).

1-[(2,6-Dichlorobenzylidene)amino]-2,2,2-trichloroethanol (5g) was synthesized by method ***A*** from chloral (4.38 g, 30.0 mmol) and 2,6-dichlorobenzaldehyde (2.69 g, 15.0 mmol) in anhydrous diethyl ether (10 mL) within 16 h in a yield of 3.57 g (72%); colorless crystals, m.p. 134—136 °C. Found (%): C, 33.84; H, 2.03; N, 4.28. $C_9H_6Cl_5NO$. Calculated (%): C, 33.63; H, 1.88; N, 4.36. ^{1}H NMR ($CDCl_3$), δ: 3.94 (br.s, 1 H, OH); 5.41 (s, 1 H, O—CH—N=); 7.20—7.24 (m, 1 H, H_{Ar}); 7.28—7.31 (m, 2 H, H_{Ar}); 8.87 (s, 1 H, CH=N). ^{13}C NMR (DMSO-d_6), δ: 95.63 (N—CH—O); 102.64 (quatern., CCl_3); 129.57; 129.83; 128.45; 129.83 (quatern.); 132.32; 132.48 (quatern.); 134.26; 159.57 (C=N). IR, ν/cm^{-1}: 1585, 1660 (C=N), 2600—3400 (bonded, OH).

1-[(3,5-Dimethyl-1-phenyl-1*H*-pyrazol-4-yl)methylideneamino]-2,2,2-trichloroethanol (5h) was synthesized by method ***A*** from chloral (0.81 g, 10.3 mmol) and 3,5-dimethyl-1-phenyl-1*H*-pyrazole-4-carboxaldehyde (1.01 g, 5.04 mmol) in anhydrous benzene (12 mL) in the presence of a catalytic amount of *p*-toluenesulfonic acid within 21 h in a yield of 1.35 g (78%); colorless crystals, m.p. 159—162 °C. Found (%): C, 48.40; H, 4.14; N, 12.23. $C_{14}H_{14}Cl_3N_3O$. Calculated (%): C, 48.51; H, 4.07; N, 12.12. ^{1}H NMR ($CDCl_3$), δ: 2.49 (s, 3 H, CH_3); 2.52 (s, 3 H, CH_3); 3.69 (br.s, 1 H, OH); 5.07 (s, 1 H, O—CH—N=); 7.41—7.44 (m, 3 H, H_{Ar}); 7.50 (m, 2 H, H_{Ar}); 8.57 (s, 1 H, CH=N). ^{13}C NMR (DMSO-d_6), δ: 11.60 (CH_3); 13.43 (CH_3); 95.29 (N—CH—O); 104.12 (quatern., CCl_3); 115.67 (quatern.); 125.36, 128.45; 129.86; 139.11 (quatern.); 142.23 (quatern.); 149.73 (quatern.); 159.80 (C=N). IR, ν/cm^{-1}: 1500, 1600, 1640 (C=N), 2800—3300 (bonded, OH). MS, m/z (I_{rel} (%)): 228 $[M - CCl_3]^{+\cdot}$ (30), 198 $[M - CCl_3CHOH]^{+\cdot}$ (100), 77 $[C_6H_5]^{+\cdot}$ (33).

Reaction of 1-arylideneamino-2,2,2-trichloroethanols with cyclopropenone derivatives (general procedure). A solution of 2,3-diphenylcyclopropenone or 2-methyl-3-phenylcyclopropenone and 1-arylideneamino-2,2,2-trichloroethanol **5a—f** in anhydrous methanol was stirred at room temperature. In some cases, catalysis with anhydrous NH_4OAc was added. The precipitate formed was separated by filtration and washed with diethyl ether. An analytically pure sample was obtained by recrystallization from xylene.

2,2′,4,4′,5,5′-Hexaphenyl-1,1′,2,2′-tetrahydro-3*H*,3′*H*-2,2′-bipyrrole-3,3′-dione (4a) was synthesized from 2,3-diphenylcyclopropenone (208 mg, 1.0 mmol) and compound **5a** (224 mg, 0.89 mmol) in a yield of 118 mg (43%); light yellow crystals, m.p. 274—276 °C (decomp.) (*cf.* Ref. 2: m.p. 275—277 °C (decomp., xylene) and Ref. 8: 279—284 °C (sublim., DMF)).

2,2′-Bis(4-methoxyphenyl)-4,4′,5,5′-tetraphenyl-1,1′,2,2′-tetrahydro-3*H*,3′*H*-2,2′-bipyrrole-3,3′-dione (4b) was synthesized from 2,3-diphenylcyclopropenone (300 mg, 1.46 mmol) and compound **5b** (376 mg, 1.33 mmol) in anhydrous methanol (5 mL) in the presence of anhydrous NH_4OAc (100 mg,

1.3 mmol) in a yield of 340 mg (75%); light yellow crystals, m.p. 278—282 °C (decomp.) (*cf.* Ref. 2: m.p. 278—281 °C (decomp., xylene) and Ref. 8: m.p. 282—285 °C (benzene)). The spectral data correspond to the published[2] values.

2,2´-Bis(4-methylphenyl)-4,4´,5,5´-tetraphenyl-1,1´,2,2´-tetrahydro-3*H*,3´*H*-2,2´-bipyrrole-3,3´-dione (4c) was synthesized from 2,3-diphenylcyclopropenone (208 mg, 1.0 mmol) and compound **5c** (271 mg, 1.0 mmol) in anhydrous methanol (5 mL) in the presence of anhydrous NH_4OAc (203 mg, 2.6 mmol) within 21 h in a yield of 212 mg (65%); light yellow crystals, m.p. 260—261 °C (decomp.) (*cf.* Ref. 2: m.p. 260—262 °C (decomp., xylene) and Ref. 8: m.p. 269—271 °C (benzene)). The spectral data correspond to the published[2] values.

2,2´-Bis(4-nitrophenyl)-4,4´,5,5´-tetraphenyl-1,1´,2,2´-tetrahydro-3*H*,3´*H*-2,2´-bipyrrole-3,3´-dione (4d) was synthesized from 2,3-diphenylcyclopropenone (205 mg, 1.0 mmol) and compound **5d** (267 mg, 0.90 mmol) in anhydrous methanol (4 mL) within 5 days in a yield of 75 mg (23%); light orange crystals, m.p. 274—278 °C (decomp.). Found (%): C, 74.24; H, 4.28; N, 7.90. $C_{44}H_{30}N_4O_6$. Calculated (%): C, 74.36; H, 4.25; N, 7.88. IR, ν/cm^{-1}: 1355 (symm., NO_2); 1540 (asymm., NO_2); 1585; 1610; 1645 (C=O); 3140—3400 (bonded, OH). ^{1}H and ^{13}C NMR spectra were not recorded because of low solubility of the substance in $CDCl_3$, DMSO-d_6, and HMPA-d_{18}.

2,2´-Bis(thiophen-2-yl)-4,4´,5,5´-tetraphenyl-1,1´,2,2´-tetrahydro-3*H*,3´*H*-2,2´-bipyrrole-3,3´-dione (4e) was synthesized from 2,3-diphenylcyclopropenone (204 mg, 0.99 mmol) and compound **5e** (230 mg, 0.89 mmol) in anhydrous methanol (4 mL) within 5 days in a yield of 174 mg (61%); light yellow crystals, m.p. 212—217 °C (decomp.). Found (%): C, 75.80; H, 4.58; N, 4.32. $C_{40}H_{28}N_2O_2S_2$. Calculated (%): C, 75.92; H, 4.46; N, 4.43. IR, ν/cm^{-1}: 1530; 1550; 1585; 1610; 1650 (C=O); 3130—3380 (bonded, OH). ^{1}H and ^{13}C NMR were not recorded because of low solubility of the substance in $CDCl_3$, DMSO-d_6, and HMPA-d_{18}. Compound **4e** was also obtained in a yield of 39% (124 mg) from 2,3-diphenylcyclopropenone (208 mg, 1.0 mmol) and compound **5e** (263 mg, 1.0 mmol) in anhydrous MeOH (5 mL) in the presence of anhydrous NH_4OAc (174 mg, 2.3 mmol) within 2 h.

2,2´-Bis(pyridin-3-yl)-4,4´,5,5´-tetraphenyl-1,1´,2,2´-tetrahydro-3*H*,3´*H*-2,2´-bipyrrole-3,3´-dione (4f) was synthesized from 2,3-diphenylcyclopropenone (207 mg, 1.0 mmol) and compound **5f** (226 mg, 0.89 mmol) in anhydrous methanol (4 mL) within 7 days in a yield of 75 mg (27%); light yellow crystals, m.p. 255—258 °C (decomp.). Found (%): C, 80.98; H, 4.90; N, 8.90. $C_{42}H_{30}N_4O_2$. Calculated (%): C, 81.01; H, 4.86; N, 9.00. IR, ν/cm^{-1}: 1520; 1545; 1585; 1610; 1645 (C=O); 3110—3400 (bonded, OH). ^{1}H and ^{13}C NMR spectra were not recorded because of low solubility of the substance in $CDCl_3$, DMSO-d_6, and HMPA-d_{18}.

2,2´-Bis(4-methoxyphenyl)-5,5´-dimethyl-4,4´-diphenyl-1,1´,2,2´-tetrahydro-3*H*,3´*H*-2,2´-bipyrrole-3,3´-dione (7b) was synthesized from 2-methyl-3-phenylcyclopropenone (144 mg, 1.0 mmol) and compound **5b** (281 mg, 1.0 mmol) in anhydrous methanol (4 mL) in the presence of anhydrous NH_4OAc (105 mg, 1.4 mmol) within 19 h in a yield of 84 mg (33%); light yellow crystals, m.p. 264—266 °C (decomp.). An analytically pure sample was washed with DMF and then with acetonitrile and diethyl ether. Found (%): C, 77.33; H, 5.62; N, 5.18. $C_{36}H_{32}N_2O_4$. Calculated (%): C, 77.68; H, 5.79; N, 5.03. MS, *m*/*z* (I_{rel} (%)): 279 $[C_{18}H_{17}NO_2]^+$ (81), 277 $[C_{18}H_{15}NO_2]^+$ (41), 264 $[C_{17}H_{14}NO_2]^+$ (45), 116 $[C_6H_5C{\equiv}CCH_3]^+$ (100). ^{1}H NMR (DMSO-d_6—$CDCl_3$), δ: 2.01 (s, 6 H, CH_3); 3.66 (s, 6 H, OMe); 6.70 (d, 4 H, H_{Ar}, J = 8.8 Hz); 6.91 (d, 4 H, H_{Ph}, J = 7.3 Hz); 7.04 (t, 2 H, H_{Ph}, J = 7.6 Hz); 7.16 (t, 4 H, H_{Ph}, J = 7.4 Hz); 7.79 (d, 4 H, H_{Ar}, J = 8.8 Hz); 8.43 (s, 2 H, NH). ^{1}H NMR NOE (DMSO-d_6—$CDCl_3$), additional irradiation at the proton frequency δ 9.37 (NH) δ: 2.11 (CH_3, 7.5%); 7.82 (H_{Ar}-*meta* to MeO group, 6.3%). IR, ν/cm^{-1}: 1610; 1640 (C=O), 3150—3400 (bonded, OH).

5,5´-Dimethyl-2,2´-bis(4-nitrophenyl)-4,4´-diphenyl-1,1´,2,2´-tetrahydro-3*H*,3´*H*-2,2´-bipyrrole-3,3´-dione (7d) was synthesized from 2-methyl-3-phenylcyclopropenone (287 mg, 2.0 mmol) and compound **5d** (594 mg, 2.0 mmol) in anhydrous methanol (3 mL) within 5 days in a yield of 247 mg (42%); yellowish-orange crystals, m.p. 284—285 °C (decomp., from xylene). Found (%): C, 69.50; H, 4.53; N, 9.56. $C_{34}H_{26}N_4O_6$. Calculated (%): C, 69.62; H, 4.47; N, 9.55. MS, *m*/*z* (I_{rel} (%)): 294 $[C_{17}H_{14}N_2O_3]^+$ (60), 292 $[C_{17}H_{12}N_2O_3]^+$ (17), 116 $[C_6H_5C{\equiv}CCH_3]^+$ (100). IR, ν/cm^{-1}: 1360 (symm., NO_2); 1470; 1550 (asymm., NO_2); 1610; 1640 (C=O), 3000—3400 (bonded, OH). ^{1}H and ^{13}C NMR spectra were not recorded because of low solubility of the substance in $CDCl_3$, DMSO-d_6, and HMPA-d_{18}.

***N*,*N*´-Bis(4-nitrobenzylidene)-1-(4-nitrophenyl)methanediamine (1d).** A solution of compound **5d** (228 mg, 0.77 mmol) in anhydrous benzene (10 mL) was refluxed for 8.5 h with stirring, the solvent was removed, and the residue was suspended in diethyl ether and filtered off. Compound **1d** was obtained in a yield of 92 mg (84%); bright yellow crystals, m.p. 148—151 °C (decomp., from benzene) (*cf.* Ref. 5: m.p. 154 °C (benzene), Ref. 9: m.p. 140 °C (acetonitrile), and Ref. 10: m.p. 75 °C (aqueous methanol)). Found (%): C, 58.92; H, 3.34; N, 16.49. $C_{21}H_{15}N_5O_6$. Calculated (%): C, 58.20; H, 3.49; N, 16.16. ^{1}H NMR ($CDCl_3$), δ: 6.19 (s, 1 H, N—CH—N); 7.72 (d, 2 H, H_{Ar}, J = 8.6 Hz); 8.05 (d, 4 H, H_{Ar}, J = 8.6 Hz); 8.29 (d, 2 H, H_{Ar}, J = 8.6 Hz); 8.33 (d, 4 H, H_{Ar}, J = 8.6 Hz); 8.69 (s, 2 H, N=CH). IR, ν/cm^{-1}: 1360 (symm., NO_2); 1525 (asymm., NO_2); 1605 (C—C_{Ar}); 1645 (C=N).

2,4,5-Tris(4-nitrophenyl)-1*H*-imidazole (6). Dry ammonia was passed through a solution of chloral (3.78 g, 25.7 mmol), 4-nitrobenzaldehyde (4.0 g, 26.5 mmol), and catalytic amount of *p*-toluenesulfonic acid in anhydrous diethyl ether (18 mL) cooled to −20—−15 °C with vigorous stirring maintaining the reaction temperature below 0 °C, after which the mixture was stirred for 90 h at room temperature. A precipitate that formed was separated by filtration, and an additional portion of the product was isolated from the mother liquor after evaporation of the solvent and washing the residue with a small amount of diethyl ether. An analytically pure sample was obtained by recrystallization from chloroform. Compound **6** was obtained in a yield of 2.44 g (32%); yellow crystals, m.p. 204—205 °C ($CHCl_3$) (*cf.* Ref. 11: m.p. 321—323 °C (aqueous pyridine) and Ref. 12: m.p. 331—334 °C (aqueous pyridine)). Found (%): C, 58.43; H, 2.85; N, 16.20. $C_{34}H_{26}N_4O_6$. Calculated (%): C, 58.47; H, 3.04; N, 16.24. ^{1}H NMR ($CDCl_3$), δ: 5.78 (br.s, 1 H, NH); 7.20 (d, 4 H, H_{Ar}, J = 8.6 Hz); 7.97 (d, 4 H, H_{Ar}, J = 8.7 Hz); 8.20 (d, 2 H, H_{Ar}, J = 9.1 Hz); 8.41 (d, 2 H, H_{Ar}, J = 9.1 Hz). IR, ν/cm^{-1}: 1530 (C—C_{Ar}); 1605 (C—C_{Ar}); 3420 (NH). MS, *m*/*z* (I_{rel} (%)): 431 $[M]^+$ (5.5), 283 $[M - O_2NC_6H_4C{\equiv}N]^+$ (14), 102 $[C_6H_4CN]^+$ (41), 76 $[C_6H_4]^+$ (100), 63 (91), 51 (94), 39 (65).

Product **6** is also formed by refluxing of compound **5d** (1.00 g, 3.4 mmol) in benzene within 18 h in a yield of 61% (330 mg).

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