UNEXPECTED COURSE OF THE REACTION OF 1,3-BIS(DIMETHYLAMINO)TRIMETHINIUM PERCHLORATE WITH 3-SUBSTITUTED PROP-2-YNALS LEADING TO 1-ARYL-2,4,6-TRIFORMYLBENZENES

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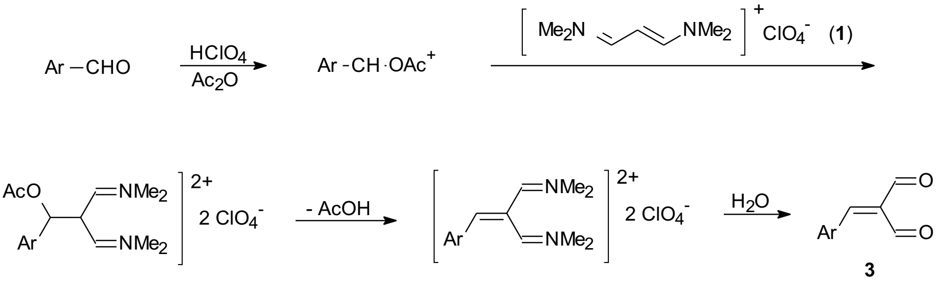
Reaction of 1,3-bis(dimethylamino)trimethinium perchlorate (**1**) with 3-substituted prop-2-ynals (**4**) in acetic anhydride at the presence of $ZnBr_2$ gives upon hydrolysis 1-substituted 2,4,6-triformylbenzenes (**6**) in low to moderate yield. This reaction is restricted to prop-2-ynals bearing electron rich aromatic substituents at the 3-position.

Key words: Trimethinium salts; Prop-2-ynals; Triformylbenzenes; Biaryls; Benzene ring construction; Cyclization.

We have previously demonstrated that the reaction of 1,3-bis(dimethylamino)trimethinium perchlorate (**1**) with aromatic aldehydes in acetic anhydride in the presence of perchloric or Lewis acids affords bis-iminium salts **2**, which can be subsequently hydrolyzed to the (arylmethylidene)malonaldehydes **3** (Scheme 1, ref.[1]). Heteroaromatic aldehydes[2], vinylogues of aromatic aldehydes[2] and polyenals with at least two double bonds in conjugation with the aldehyde group[3] behave similarly.



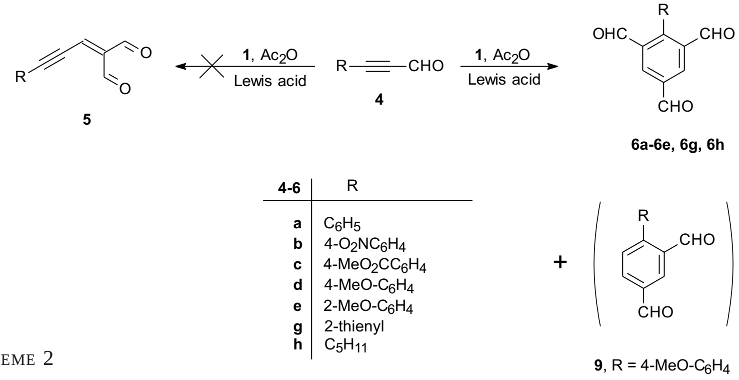
2

3

SCHEME 1

The proposed mechanisms of this reaction involves reaction of aromatic aldehyde with acetic anhydride, electrophilic attack of formed carbocation to the trimethinium salt and finally formation of the bis-iminium salt **2** by elimination of acetic acid[1] (Scheme 1). Bis-iminium salt **2** was in some cases isolated and characterized[2].

We supposed, that 3-phenylprop-2-ynal (**4a**) would react with perchlorate **1** analogously to the vinylogues of benzaldehyde under the formation of (alkynylmethylene)malonaldehyde **5**. Such a compound would serve as a valuable starting material for the synthesis of heterocycles[4] and substituted malonaldehydes[5,6]. However, the reaction of **4a** with 1,3-bis(dimethylamino)trimethinium perchlorate (**1**) in acetic anhydride in the presence of $ZnCl_2$ gave a different product. Its ^{1}H NMR spectrum revealed the presence of two aldehyde groups with chemical shifts 10.20 ppm (1 H) and 9.85 ppm (2 H), together with another singlet at 9.85 ppm (2 H) and the multiplet of phenyl group. ^{13}C NMR spectrum confirmed the presence of two types of aldehyde groups (190.72 and 190.48 ppm), together with four CH groups in the aromatic region (133.41, 131.12, 130.46 and 129.58 ppm) and signals of four quaternary carbons (152.9, 136.75, 136.46 and 132.25 ppm). These spectra are in agreement with the structure of 1-phenyl-2,4,6-triformylbenzene (**6a**) (Scheme 2). The structure was further confirmed by mass spectrometry, which contained the expected molecular peak M^+ (*m/z* 238) and the fragments formed by stepwise losing three formyl groups.



5

4

6a-6e, 6g, 6h

9, R = 4-MeO-C_6H_4

4-6	R
a	C_6H_5
b	4-$O_2NC_6H_4$
c	4-$MeO_2CC_6H_4$
d	4-MeO-C_6H_4
e	2-MeO-C_6H_4
g	2-thienyl
h	C_5H_{11}

SCHEME 2

The yield of trialdehyde **6a** was rather low (17%). Therefore we attempted to optimize the reaction conditions using HPLC analysis for the determination of the yield. The trialdehyde **6a** was evidently formed from one molecule of the 3-phenylprop-2-ynal (**4a**) and two molecules of the trimethinium salt **1**. Therefore we used the 1 : 2.5 molar ratio of aldehyde **4a** to **1** in further experiment. To our surprise, the yield of trialdehyde **6a** was even lower in this case. For that reason the following experiments were done with slight excess of **4a** (1.3 : 1 molar ratio).

Further experiments showed, that $ZnBr_2$ was slightly more efficient than $ZnCl_2$, while $BF_3 \cdot Et_2O$ and $HClO_4$ were completely ineffective. From our earlier study it has been known, that instead of acetic anhydride also pivaloyl chloride (PivCl) or trifluoroacetic anhydride (TFAA) can be used for the reaction of aromatic aldehydes with trimethinium perchlorate. In our case, the reaction in trifluoroacetic anhydride did not proceed at all. With pivaloyl chloride the desired trialdehyde **6a** was formed together with impurities which were not possible to separate. The yield of **6a** was slightly higher than that with acetic anhydride. Prolongation of the reaction time and enhancing the temperature influenced the yield of the reaction only negligibly. It has been known that instead of aromatic aldehydes, also their acetals or acetates can be used for the preparation of arylmethylidenemalonaldehydes[3]. However, the reaction of diethyl acetal or diacetate of 3-phenylprop-2-ynal with perchlorate **1** in acetic anhydride in the presence

TABLE I
reaction of 3-phenylprop-2-ynal (**4a**) with trimethinium perchlorate **1**

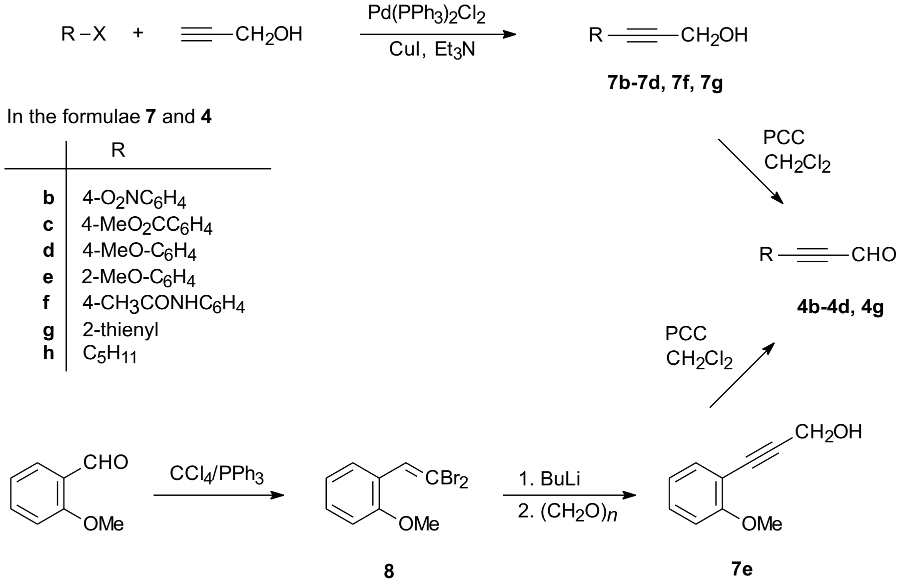
Reagent	Catalyst	Ratio **4a** : **1**	Temperature °C	Reaction time h	Yield of **6** %
Ac_2O	$ZnCl_2$	1.3 : 1	r.t.	17	17
Ac_2O	$ZnBr_2$	1.3 : 1	r.t.	17	21
Ac_2O	$BF_3 \cdot Et_2O$	1.3 : 1	r.t.	17	0
Ac_2O	$HClO_4$	1.3 : 1	r.t.	17	0
Ac_2O	$ZnBr_2$	1 : 2.5	r.t.	17	10
Ac_2O	$ZnBr_2$	1.3 : 1	r.t.	48	25
Ac_2O	$ZnBr_2$	1.3 : 1	50	17	23
Ac_2O[a]	$ZnBr_2$	1.3 : 1	r.t.	17	[b]
Ac_2O[c]	$ZnBr_2$	1.3 : 1	r.t.	17	[b]
TFAA	$ZnBr_2$	1.3 : 1	r.t.	17	0
PivCl	$ZnBr_2$	1.3 : 1	r.t.	17	>21

[a] With Ph–C≡C–$CH(OEt)_2$. [b] Traces of the product. [c] With Ph–C≡C–$CH(OAc)_2$.

of $ZnBr_2$ gave only traces of the desired trialdehyde **6a**. All these results are summarized in Table I.

The influence of the structure of starting propynal **4** on the yield of trialdehyde **6** was examined next. We chose substituents bearing electron acceptors (4-nitrophenyl and 4-methoxycarbonyl), donors (4-methoxyphenyl, 4-acetamidophenyl and sterically more demanding 2-methoxyphenyl), 2-thienyl derivative (as an example of a heteroaromatic propynal) and oct-2-ynal (as an example of an aliphatic one).

The above mentioned propynals **4** were prepared by oxidation of the corresponding alcohols **7** with pyridinium chlorochromate in CH_2Cl_2 solution. Most of the starting alcohols **4** was synthesized by Pd/CuI-catalyzed coupling of substituted arylhalides with prop-2-yn-1-ol (Scheme 3, ref.[7]).



SCHEME 3

Preparation of 2-methoxy derivative **7e** by Pd-catalyzed coupling was not successful, probably as a consequence of competing orthopalladiation[8]. Therefore, a different approach was used for the preparation of **7e**. 2-Methoxybenzaldehyde was converted to dibromo derivative **8**, which was further reacted with BuLi and paraformaldehyde furnishing the desired alcohol **7e** (Scheme 3). The oct-2-yn-1-ol (**7h**) was prepared similarly by the reaction of lithium salt of hept-1-yne with paraformaldehyde.

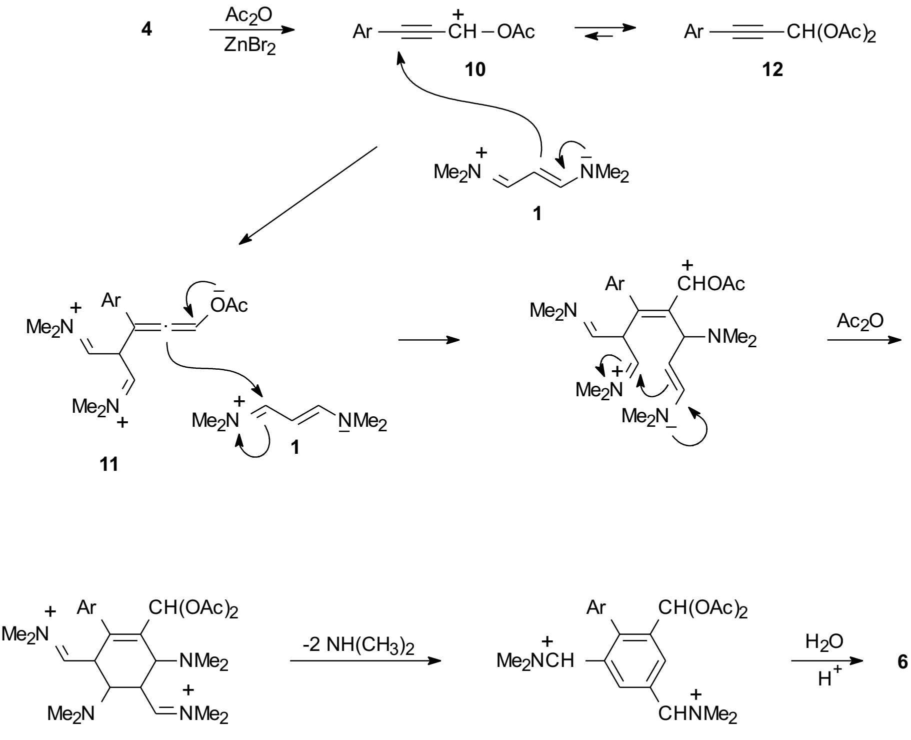
Oxidation of the alcohols **7b**–**7h** with pyridinium chlorochromate (PCC) proceeded smoothly giving low to medium yields (19–66%). We failed to obtain the 4-acetamido derivative **4f** by oxidation of the corresponding alcohol **7f**. The desired aldehyde **4f** was detected in small amount by TLC in the reaction, however, could not be isolated due to its instability. The same results as with PCC were obtained using Swern oxidation or the oxidation with active MnO_2.

The results of the reaction of 3-substituted prop-2-ynals with 1,3-bis(dimethylamino)trimethinium perchlorate (**1**) in acetic anhydride in the presence of $ZnBr_2$ are strongly dependent on the nature of the starting 3-substituted prop-2-ynal (Table II). The introduction of electron-withdrawing groups (entry 2 and 3) resulted in the formation of only traces of trialdehydes **6b** and **6c** , which could not be isolated in pure form and were detected only by ^{1}H NMR. Similar results were obtained with oct-2-ynal (entry 7). On the contrary, the presence of donor substituent (4-MeO) multiplied the yield almost twice (entry 4). In the case of 2-methoxy derivative (entry 5) the yield was somewhat lower compared to the 4-methoxy derivative, probably for the steric reasons. A relatively high yield of trialdehyde was also obtained with 2-thienyl derivative **4g** (entry 6), which can also be considered as an electron-rich aromatic compound. In several cases, the presence of a small amount of another, less polar product was observed. This side-product was isolated from the reaction of 3-(4-methoxyphenyl)prop-2-ynal with **1**. Using ^{1}H, ^{13}C NMR and MS spectra, this by-product was identified as the dialdehyde **9**. Formation of this compound can be explained by decarbonylation of the originally formed trialdehyde **6d** in acidic media[9].

TABLE II
Formation of 1-substituted 2,4,6-triformylbenzenes **6a**–**6h** from the reaction of 3-substituted prop-2-ynals **4** with **1** in Ac_2O in the presence of $ZnBr_2$

Entry	Product	R	Yield, %	Entry	Product	R	Yield, %
1	**6a**	C_6H_5	21	5	**6e**	2-MeO-C_6H_4	30
2	**6b**	4-O_2N-C_6H_4	<1	6	**6g**	2-thienyl	49
3	**6c**	4-MeO_2C-C_6H_4	<1	7	**6h**	$CH_3(CH_2)_4$-	<2
4	**6d**	4-MeO-C_5H_4	46				

This reaction is evidently complex and we can only speculate on its course. It seems, however, that at least some steps can be interpreted satisfactorily (Scheme 4). We presume that the first reaction step is the reaction of acetylated aldehyde **10** with the trimethinium salt in S_N2' manner. Such reactions of propargylic systems leading to allenes are common[10]. The next step is the reaction of the formed allenic enol acetate **11** with another molecule of trimethinium salt **1**, which in this case reacts as an imine. This type of reactivity of the trimethinium salts with nucleophiles such as Grignard reagents[11] has been known as well. Subsequent cyclization followed by the splitting of dimethylamine results in the formation of the aromatic system. The final product, the trialdehyde **6**, is then formed by hydrolysis during the work-up. Similar reactions have been already observed. Thus, for



SCHEME 4

example, formation of 1,3,5-triformylbenzene in the course of formylation of the heptamethinium perchlorate has been reported[12].

We assume that the cationic intermediate **10** is in equilibrium with the corresponding diacetate **12**, which in this equilibrium strongly prevails. When the trimethinium salt is not present, acetate **12** is the only product and can be isolated in high yield. Acetate **12** is very stable under reaction conditions and only traces of trialdehyde **6a** were isolated, when the acetate **12a** (Ar = Ph) instead of free aldehyde **4a** was used in the reaction with the trimethinium salt **1**. This high stability of the diacetate **12** may explain the necessity to use an excess of **4** in the reaction. Higher yields with the aldehydes bearing donor substituents on the aromatic ring can be explained by stabilization of the cationic intermediate **10** by mesomerism, resulting in its higher concentration. On the contrary, electron-withdrawing substituents destabilize the cationic intermediate **10** and the yields of trialdehydes **6** are therefore very low. The same behaviour was observed for oct-2-ynal in which mesomeric stabilization of the cation **10** is not possible and the yield of the corresponding trialdehyde **6h** is also very low.

The influence of reaction media also supports the proposed mechanisms. There is no significant difference in the yield in the preparation of (arylmethylidene)malonaldehydes if the reaction is run in acetic anhydride, pivaloyl chloride or trifluoroacetic anhydride[13]. However, the reaction of 3-phenylprop-2-ynal with 1,3-bis(dimethylamino)trimethinium perchlorate (**1**) in trifluoroacetic anhydride affords only traces of the expected trialdehyde **6a**, while the same reaction in the pivaloyl chloride gives a somewhat higher yield than in acetic anhydride. This can be rationalized as a result of an electronic effects. The enol trifluoroacetate analogous to **11** is less nucleophilic compared to the enol acetate **11** and therefore less reactive in the reaction with **1**. The opposite is true for the corresponding enol pivalate, which is more nucleophilic and therefore more reactive towards **1** than the enol acetate **11**. Moreover, formation of dipivalate is disfavoured for steric reasons and the concentration of cationic intermediate **10** should therefore be higher.

Whatever the real mechanisms of the formation of trialdehydes **6** is, it is clear that this reaction can hardly be synthetically useful. However, it serves as an interesting example of the formation of highly functionalized benzene ring from aliphatic precursors.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Unless otherwise noted, all ^{1}H NMR spectral data were recorded in $CDCl_3$ at 300 MHz, and chemical shifts are reported relative to TMS. ^{13}C NMR spectra were recorded at 75.46 MHz using APT technique. HPLC analyses were run on LiChrosfer 100 RP-18 in methanol–water mixture. IR spectra were measured in $CHCl_3$. Tetrahydrofuran was distilled from benzophenone ketyl under the nitrogen prior to use. 3-Phenylprop-2-ynal diethyl acetal[14], 3-phenylprop-2-ynal[15], 3-(4-methoxyphenyl)prop-2-ynal[16], 3-(2-thienyl)prop-2-yn-1-ol[7], oct-2-ynal[17] and 1,3-bis(dimethylamino)trimethinium perchlorate[18] were prepared according to the reported procedures.

Diacetate of 3-Phenylprop-2-ynal

$ZnBr_2$ (0.3 g, 1.33 mmol) was dissolved in acetic anhydride (10 ml) at 60 °C, the solution was then cooled in ice bath and 3-phenylprop-2-ynal (1.0 g, 7.7 mmol) was added under stirring. After 10 min, the reaction mixture was poured into 5% K_2CO_3 (100 ml) and extracted with diethyl ether (3 × 50 ml). The combined extracts were washed with 5% K_2CO_3, dried over $MgSO_4$, the solvent was evaporated *in vacuo* and the residue was destilled. The product was obtained as an oil (1.0 g, 56%), b.p. 150 °C/3 Pa (bath temperature). ^{1}H NMR spectrum: 2.20 s, 6 H (2 × CH_3); 7.35 m, 3 H (ArH); 7.50 m, 2 H (ArH). For $C_{13}H_{12}O_4$ (232.2) calculated: 67.23% C, 5.20% H; found: 67.06% C, 5.21% H.

3-(4-Nitrophenyl)prop-2-yn-1-ol (**7b**)

To a mixture of triethylamine (4 ml, 54 mmol), $PdCl_2(PPh_3)_2$ (0.140 g, 0.2 mmol), CuI (0.08 g, 0.4 mmol), 4-iodotoluene (5.13 g, 23.5 mmol), $CHCl_3$ (40 ml) and *N*-methylpyrrolidin-2-one (20 ml) prop-2-en-1-ol (1.5 ml, 25.8 mmol) was added *via* syringe under argon. After stirring overnight the mixture was poured into water (250 ml), extracted with diethyl ether (3 × 200 ml), the combined ether extracts were washed with water (4 × 150 ml), dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. Chromatography on silica (CH_2Cl_2) gave 2.96 g (81%) of the product, m.p. 94.5–96 °C (ref.[19] gives 95–96.5 °C).

3-(4-Methoxycarbonylphenyl)prop-2-yn-1-ol (**7c**)

A mixture of methyl 4-bromobenzoate (13 g, 60.4 mmol), $PdCl_2(PPh_3)_2$ (1.0 g, 1.4 mmol), CuI (1.0 g, 5.25 mmol), PPh_3 (0.8 g, 3 mmol) and prop-2-en-1-ol (4.1 ml, 20.4 mmol) in triethylamine (80 ml) was refluxed under argon for 1 h. After cooling the reaction mixture was diluted with diethyl ether (200 ml), the separated triethylamine hydroiodide was filtered off, washed with diethyl ether and the solvents were evaporated *in vacuo*. The residue was dissolved in benzene and washed successively with H_2O, diluted hydrochloric acid and brine. After drying over $MgSO_4$, the solution was filtered through a short pad of silica, the silica was washed with dichloromethane, and the solvents from combined filtrates were evaporated *in vacuo*. Crystallization from a mixture of toluene (50 ml) and heptane (30 ml) afforded 9.31 g (81%) of the product, m.p. 79–80 °C (ref.[20] gives 79–81 °C).

3-(4-Methoxyphenyl)prop-2-yn-1-ol (**7d**)

To a mixture of 1-iodo-4-methoxybenzene (5.85 g, 25 mmol), $PdCl_2(PPh_3)_2$ (0.085 g, 0.12 mmol), CuI (0.1 g, 0.52 mmol), triethylamine (10 ml) and $CHCl_3$ (25 ml) prop-2-en-1-ol (1.6 ml, 27.5 mmol) was added under argon and the mixture was stirred at 40 °C overnight. The solvents were then evaporated, the residue mixed with diethyl ether (100 ml), the separated triethylamine hydroiodide was filtered off and washed with diethyl ether (3 × 50 ml). The solvent was then evaporated and chromatography of the residue on silica (CH_2Cl_2) gave pure product 1.83 g (45%), m.p. 59–61.5 °C, (ref.[21] gives 62 °C).

3-(2-Methoxyphenyl)prop-2-yn-1-ol (**7e**)

1-(2,2-Dibromovinyl)-2-methoxybenzene[22] (6.49 g, 22.2 mmol) was dissolved in dry THF (50 ml), the solution was cooled to –78 °C and 1.5 M solution of butyllithium (34 ml, 51 mmol) was added. The solution was stirred for 1 h at –78 °C, and then paraformaldehyde (2 g, 667 mmol) was added. The mixture was left at –78 °C for 10 min, then it was allowed to warm to room temperature and stirred for another hour. The reaction mixture was quenched with solution of NaCl (80 ml), the product was extracted with diethyl ether (3 × 150 ml) and the combined extracts were dried over $MgSO_4$. Evaporation of the solvents *in vacuo* gave crude product, which was purified by chromatography (silica, light petroleum–ethyl acetate 2 : 1), 2.32 g (65%), m.p. 62.5–63 °C. ^1H NMR: 3.89 s, 3 H (OCH_3); 4.55 s, 2 H (CH_2); 6.90 m, 2 H (ArH); 7.31 m, 1 H (ArH); 7.42 m, 1 H (ArH). IR: 3 016 (m), 1 597 (w), 1 576 (w), 1 498 (s), 1 465 (m), 1 435 (m), 1 264 (s). For $C_{10}H_{10}O_2$ (162.2) calculated: 74.06% C, 6.21% H; found: 73.97% C, 6.50% H.

3-(4-Acetamidophenyl)prop-2-yn-1-ol (**7f**)

To the mixture of 4-acetamido-1-iodobenzene (6.5 g, 25 mmol), triethylamine (5 ml, 36 mmol), $PdCl_2(PPh_3)_2$ (0.68 g, 1 mmol) and CuI (0.4 g, 2.1 mmol) in $CHCl_3$ (25 ml) prop-2-en-1-ol (5 ml, 36 mmol) was added *via* syringe under argon and the mixture was stirred for 30 h at 40 °C. The product was extracted with ethyl acetate from the solid formed in the course of the reaction and crystallized from ethyl acetate–light petroleum mixture. The yield was 2.0 g (43%), m.p. 159–160 °C. ^1H NMR (DMSO-d_6): 2.04 s, 3 H (CH_3); 4.27 d, 2 H, $J = 6$ (CH_2); 5.28 t, 1 H, $J = 6$ (OH); 7.34 d, 2 H, $J = 7$ (ArH); 7.58 d, 2 H, $J = 7$ (ArH). IR (KBr): 1 658 (s), 1 600 (s), 1 538 (s), 1 500 (s), 1 401 (m), 1 366 (s), 1 326 (s). For $C_{11}H_{11}NO_2$ (189.2) calculated: 69.83% C, 5.86% H, 7.40% N; found: 69.64% C, 5.96% H, 7.20% N.

General Procedure for the Preparation of Propynals **4b**–**4e**, **4g** and **4h**

To a stirred solution of propynol **7** (11 mmol) in dry dichloromethane (100 ml) a mixture of PCC (4.7 g, 22 mmol) and dry celite (4.7 g) was added in portions during 2 h. The mixture was stirred for another hour and filtered through a thin layer of silica gel to remove polar impurities. The solvent was evaporated and the residue purified by chromatography on silica gel.

3-(4-Nitrophenyl)prop-2-ynal (**4b**). Eluent: light petroleum–diethyl ether (3 : 2), yield 60%, m.p. 121–123 °C (ref.[23] gives 123–123.5 °C).

3-(4-Methoxycarbonylphenyl)prop-2-ynal (**4c**). Crystallization of crude product from heptane (60 ml) gave pure **4c** in 64% yield, m.p. 88–89 °C. ^1H NMR: 3.94 s, 3 H (CH_3); 7.66 d, 2 H,

J = 9 (ArH); 8.07 d, 2 H, J = 9 (ArH); 9.45 s, 1 H (CHO). ^{13}C NMR: CH, CH_3: 177.08, 133.66, 130.38, 53.14; C: 166.59, 132.87, 124.48, 93.67, 90.32. IR ($CHCl_3$): 3 022, 2 193, 1 724, 1 663, 1 607, 1 437, 1 280. For $C_{11}H_8O_3$ (188.2) calculated: 70.21% C, 4.28% H; found: 69.72% C, 4.47% H.

*3-(4-Methoxyphenyl)prop-2-ynal (*4d). Eluent: CH_2Cl_2, yield 35%, m.p. 47–48 °C (ref.[16] gives 47–48.5 °C).

3-(2-Methoxyphenyl)prop-2-ynal (**4e**). Eluent: light petroleum–acetone–diethyl ether 8 : 1 : 1, yield 40%. The product was obtained as an oil. ^{1}H NMR : 3.91 s, 3 H (OCH_3); 6.95 m, 2 H (ArH); 7.50 m, 2 H (ArH); 9.45 s, 1 H (CHO). IR: 3 022, 2 841, 2 185, 1 657, 1 597, 1 492, 1 270. For $C_{10}H_8O_2$ (160.2) calculated: 74.99% C, 5.03% H; found: 74.87% C, 5.35% H.

3-(2-Thienyl)prop-2-ynal[24] (**4g**). Eluent: light petroleum–ethyl acetate 95 : 5, yield 25%, m.p. 33–36 °C. ^{1}H NMR: 7.10 m, 1 H (ThH); 7.55 m, 2 H (ThH); 9.40 s, 1 H (CHO). ^{13}C NMR: CH, CH_3: 176.63, 138.13, 133.30, 128.56; C: 119.80, 93.83, 89.82.

General Procedure for the Preparation of Trialdehydes **6**

In a 250-ml flask $ZnBr_2$ (0.5 g) was dissolved in acetic anhydride (5 ml) at 60 °C. The solution was cooled in an ice bath and 1,3-bis(dimethylamino)trimethinium perchlorate (**1**; 0.452 g, 2 mmol) was added followed by prop-2-ynal **4** (2.6 mmol). The mixture was stirred with ice-cooling for 1 h and then without cooling for another 17 h. Dry ether (200 ml) was added and the mixture was intensively stirred for 1 h. The separated oil or solid was washed twice with an excess of dry ether. Then water (100 ml), benzene (40 ml) and dichloromethane (10 ml) were added and the mixture was stirred for 1 h. The organic layer was separated and the aqueous one was extracted twice with ether (50 ml). The combined extracts were dried over magnesium sulfate, and filtered through a thin layer of silica gel to remove polar impurities. The solvents were evaporated *in vacuo* and the residue purified by chromatography on silica gel (Chromatotron, 2 mm plate, CH_2Cl_2 or CH_2Cl_2–light petroleum mixture). The yields are listed in Table II.

Biphenyl-2,4,6-tricarbaldehyde (**6a**). M.p. 159–160 °C. ^{1}H NMR: 7.60 m 3 H (ArH); 7.41 m, 2 H (ArH); 8.72 s, 2 H (ArH); 9.86 s, 2 H (CHO); 10.21 s, 1 H (CHO). ^{13}C NMR: CH: 190.48, 190.72, 130.46, 131.12, 133.41, 129.58; C: 132.25, 136.46, 136.75, 152.9. IR: 3 026, 2 871, 1 710, 1 691, 1 595, 1 566, 1 423, 1 375. Mass spectrum, *m/z*: 238 (M^+), 209 (M^+ – CO), 181 (M^+ – 2 CO), 152 (M^+ – 3 CO). For $C_{15}H_{10}O_3$ (238.2) calculated: 75.62% C, 4.23% H; found: 75.37% C, 4.28% H.

4'-Nitrobiphenyl-2,4,6-tricarbaldehyde (**6b**). ^{1}H NMR: 7.62 d, 2 H, J = 9 (ArH); 8.46 d, 2 H, J = 9 (ArH); 8.75 s, 2 H (ArH); 9.85 s, 2 H (CHO); 10.24 s, 1 H (CHO).

4'-(Methoxycarbonyl)biphenyl-2,4,6-tricarbaldehyde (**6c**). ^{1}H NMR: 4.00 s, 3 H (CO_2CH_3); 7.51 d, 2 H, J = 8 (ArH); 8.26 d, 2 H, J = 8 (ArH); 8.74 s, 2 H (ArH); 9.83 s, 2 H (CHO); 10.22 s, 1 H (CHO).

4'-Methoxybiphenyl-2,4,6-tricarbaldehyde (**6d**). M.p. 138–140 °C. ^{1}H NMR: 3.92 s, 3 H (OCH_3); 7.09 d, 2 H, J = 9 (ArH); 7.31 d, 2 H, J = 9 (ArH); 8.70 s, 2 H (ArH); 9.90 s, 2 H (CHO); 10.20 s, 1 H (CHO). ^{13}C NMR: CH, CH_3: 190.82, 190.78, 133.48, 132.69, 115.08, 56.21; C: 161.50, 152.81, 136.70, 136.43, 123.98. IR: 3 026, 2 841, 1 709, 1 692, 1 601, 1 515, 1 254. For $C_{16}H_{12}O_4$ (268.3) calculated: 71.64% C, 4.51% H; found: 71.19% C, 4.87% H.

4'-Methoxybiphenyl-2,4-dicaboxaldehyde (**9**). This compound was isolated as the first fraction during isolation of **6d**. Yield 15%, m.p. 99–103 °C. ^{1}H NMR: 3.91 s, 3 H (OCH_3); 7.07 m, 2 H (ArH); 7.37 m, 2 H (ArH); 7.64 d, 1 H, J = 8 (ArH); 8.13 dd, 1 H, J = 8, J' = 2

(ArH); 8.50 d, 1 H, *J* = 2 (ArH). ^{13}C NMR: CH, CH_3: 192.13, 191.78, 132.89, 132.39, 131.98, 131.38, 114.98, 56.13; C: 161.14, 151.47, 135.83, 134.81, 129.37. IR: 3 028, 2 841, 1 701, 1 606, 1 518, 1 251. HR MS M^+: *m/z* for $C_{15}H_{12}O_3$ calculated: 240.0786; found: 240.0792.

2'-(Methoxycarbonyl)biphenyl-2,4,6-tricarbaldehyde (**6e**). M.p. 166–167 °C. ^{1}H NMR: 3.76 s, 2 H (OCH_3); 7.06–7.25 m, 3 H (ArH); 7.56 m, 1 H (ArH); 8.71 s, 2 H (ArH); 9.79 s, 2 H (CHO); 10.19 s, 1 H (CHO). ^{13}C NMR: CH, CH_3: 190.92, 133.20, 132.95, 132.52, 121.71, 111.77, 56.28; C: 157.44, 149.43, 136.60, 136.50, 120.74. IR: 3 024, 2 841, 1 709, 1 690, 1 601, 1 464, 1 255. For $C_{16}H_{12}O_4$ (268.3) calculated: 71.64% C, 4.51% H; found: 71.41% C, 4.68% H.

1-(2-Thienyl)benzene-2,4,6-tricarbaldehyde (**6g**). M.p. 122–123 °C. ^{1}H NMR : 7.25 m, 2 H (3,4-ThH); 7.67 dd, 1 H, *J* = 1, J' = 5 (5-ThH); 8.66 s, 2 H (ThH); 9.98 s, 2 H (CHO); 10.18 s, 1 H (CHO). ^{13}C NMR: CH: 190.57, 190.05, 133.10, 132.67, 130.26, 128.73; C: 145.12, 137.61, 137.19, 131.72. IR: 3 023, 2 867, 1 712, 1 691, 1 596, 1 567, 1 424, 1 374. For $C_{13}H_8O_3S$ (244.3) calculated: 63.92% C, 3.30% H; found: 63.61% C, 3.48%.

1-(1-Pentyl)benzene-2,4,6-tricarbaldehyde (**6h**). ^{1}H NMR: 0.8–1.7 m, 9 H ($CH_3(CH_2)_3$); 3.54 m, 2 H ($ArCH_2$); 8.57 s, 2 H (ArH); 10.13 s, 1 H (CHO); 10.46 s, 2 H (CHO).

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