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Reduction of Tri(hetero)arylcarbinols to Tri(hetero)arylmethanes

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Summary. A series of seven new tri(hetero)arylmethanes has been prepared by reduction of the corresponding carbinols using a mixture of lithium aluminium hydride/aluminium trichloride. The yields are excellent (77–98%) except in the case of the tri(2-benzothienyl)derivative (41%). ^{1}H NMR spectra are discussed.

Keywords. Tri(hetero)arylcarbinols; Tri(hetero)arylmethanes.

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Zusammenfassung. Durch die Reduktion der entsprechenden Carbinole mit Lithium-aluminiumhydrid/Aluminiumchlorid wurden sieben neue Tri(hetero)arylmethane in sehr guten Ausbeuten (77–98%) hergestellt. Eine Ausnahme bildet das Tri-(2-benzothienyl)-Derivat mit 41%. Die ^{1}H-NMR-Spektren werden diskutiert.

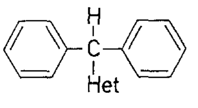
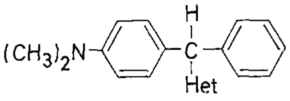
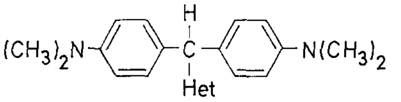
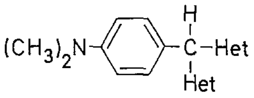
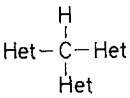
Introduction

Recently we reported the synthesis of tri(hetero)arylcarbonium salts as heterocyclic analogues of triarylmethane dyes by acid treatment of the corresponding tri(hetero)arylcarbinols [1, 2]. Some of these carbinols also showed a high reactivity against nucleophiles [3]. The present work represents a further extension of the reactivity studies, reporting the reduction of some representative carbinols.

Results and Discussion

Preliminar experiments on (2-thienyl)diphenylcarbinol using $LiAlH_4/AlCl_3$, Zn/*Ac*OH and HI/*Ac*OH as reduction systems, showed that the first one could give **1** in quantitative yield (Table 1). This result contrasted with the 50% yield reported for a similar reduction using formic acid [4]. The Zn/*Ac*OH system afforded the lower yields in an order similar to that described in the synthesis of **2** from the corresponding carbinol [5]. The efficiency of the $LiAlH_4/AlCl_3$ reducing system was also showed with other (heteroaryl) diphenylcarbinols to give the methanes **2**–**6** as well as with (diheteroaryl) phenyl- and triheteroarylcarbinols to give

Table 1. Synthesis of compounds **1**–**8**

Compound	No.	Het	Reduction	Yield (%)
	**1**	2-thienyl	Zn/AcOH	44
			HI/AcOH	76
			$LiAlH_4/AlCl_3$	94
	2	2-benzofuryl	$LiAlH_4/AlCl_3$	77
	**3**	2-benzothienyl	$LiAlH_4/AlCl_3$	87
	4	2-benzofuryl	$LiAlH_4/AlCl_3$	98
	**5**	2-benzothienyl	$LiAlH_4/AlCl_3$	98
	6	1-methyl-2-indolyl	$LiAlH_4/AlCl_3$	97
	**7**	2-benzothienyl	$LiAlH_4/AlCl_3$	93
	**8**	2-benzothienyl	$LiAlH_4/AlCl_3$	41
			HI/AcOH	56

the methanes **7** and **8** in excellent yields in most cases (Table 1). The system $LiAlH_4/AlCl_3$ has been highly efficient in the reduction of 9-aryl-9-fluorenols to 9-arylfluorenes [6] while the reduction of tris(imidazolyl)carbinols has been unsuccessful [7].

Compound **5** has been previously obtained by reaction of benzothiopheno-2-carbaldehyde and dimethylaniline [8].

The proton NMR spectra in deuterochloroform of the tri(heteroaryl)arylmethanes have been recorded for identification (see Experimental Part). The signal of the CH proton is sensitive to the nature of the aryl (heteroaryl) residues. Taking triphenylmethane ($\delta = 5.60$) as reference, the contribution of the other groups is clearly additive ($r^2 = 0.99$): *p*-dimethyl-aminophenyl, -0.11 ppm, 2-thienyl, $+0.12$ ppm, 2-(1′-methyl)indolyl, $+0.11$ ppm, 2-benzofuryl, 0.00 ppm, and 2-benzothienyl, $+0.21$ ppm. These values result from electronic [2] and anisotropic effects.

Experimental Part

Melting points: Büchi capillary melting point apparatus. IR-Spectra: Perkin-Elmer 457 spectrophotometer. ^1H-NMR-spectra: Perkin-Elmer R 24-B (60 MHz), $CDCl_3$ as solvent, shifts in ppm relative to *TMS*.

Method A. Reduction with Zn/*Ac*OH

A mixture of 5 g Zn powder, 15 ml *Ac*OH and 0.001 mol of the corresponding carbinol was refluxed for 4 h, neutralized with $NaHCO_3$ and the evaporated residue recrystallized.

Method B. Reduction with HI/*Ac*OH

A mixture of 0.001 mol of the corresponding carbinol, 30 ml *Ac*OH and 4.5 ml 57% HI was refluxed for 17 h, poured on water, and extracted with diethyl ether. The organic layers were washed with aqueous $NaHSO_3$, $NaHCO_3$ and, finally, with water. The combined extracts were dried over sodium sulphate and evaporated. The solid residues were purified by crystallization.

Method C. Reduction with $LiAlH_4/AlCl_3$

To a mixture of 0.1 g (0.002 mol) $LiAlH_4$ and 0.7 g (0.005 mol) anhydrous $AlCl_3$ in 100 ml dry diethyl ether, 0.001 mol of the corresponding tri(hetero)arylcarbinol were added. After refluxing 16 h, the reaction was cooled and a mixture of ice-water was slowly added. After separation of the organic layer, the mother liquours were extracted with diethyl ether and the solid residues obtained by evaporation of the dried organic extracts were recrystallized.

(2-Thienyl)diphenylmethane (**1**)

M.p. 61–63 °C (*Et*OH) (Lit. [4]: 63 °C). ^{1}H-NMR: $\delta = 5.70$ (s, 1 H, CH), 6.70 (m, 1 H, H 4-Het), 6.90 (m, 1 H, H 3-Het), 7.20 (m, H 5-Het), 7.25 (m, Ph, overlapped signal).

(2-Benzofuryl)diphenylmethane (**2**)

M.p. 109–111 °C (*Et*OH/H_2O) (Lit. [5]: 113–114 °C). ^{1}H-NMR: $\delta = 5.55$ (s, 1 H, CH), 6.25 (s, 1 H, H 3-Het), 7.0–7.6 (m, H 4-H 7-Het), 7.25 (m, *Ph*, overlapped signal).

(2-Benzothienyl)(4-dimethylaminophenyl)methane (**3**)

M.p. 129–131 °C (*Et*OH/H_2O). IR (KBr) ν: 1 610, 1 520, 1 355, 800, 750 cm^{-1}. H-NMR: $\delta = 2.90$ (s, 6 H, N*Me*$_2$), 5.65 (s, 1 H, CH), 6.65 (d, H 2 and H 6-*p*-N*Me*$_2$C$_6$H$_4$), 7.0–7.8 (m, H 4-H 7-Het), 7.25 (m, *Ph*, overlapped signal). Anal. calcd. for $C_{23}H_{21}NS$: C 80.42, H 6.16, N 4.07. Found: C 80.21, H 6.29, N 4.42.

(2-Benzofuryl)(4-dimethylaminophenyl)phenylmethane (**4**)

M.p. 96–98 °C (*Et*OH/H_2O). IR (KBr) ν: 1 610, 1 520, 1 450, 1 345, 810, 750 cm^{-1}. ^{1}H-NMR: $\delta = 2.90$ (s, 6 H, N*Me*$_2$), 5.50 (s, 1 H, CH); 6.25 (s, 1 H, H 3-Het); 6.65 (d, 2 H, H 3 and H 5-*p*-N*Me*$_2$C$_6$H$_4$), 7.0–7.6 (m, H 4-H 7-Het), 7.10 (d, 2 H, H 2 and H 6-*p*-*Me*$_2$C$_6$H$_4$), 7.20 (m, 5 H, *Ph*). Anal. calcd. for $C_{23}H_{21}NO$: C 84.36, H 6.46, N 4.27. Found: C 84.49, H 6.31, N 4.50.

(2-Benzothienyl)bis(4-dimethylaminophenyl)methane (**5**)

M.p. 143–145 °C (*Et*OH/H_2O) (Lit. [8] 142–143 °C). ^{1}H-NMR: $\delta = 2.90$ (s, 12 H, *Me*$_2$N), 5.55 (s, 1 H, CH), 6.65 (d, H 3 and H 5-*p*-N*Me*$_2$C$_6$H$_4$), 6.90 (s, 1 H, H 3-Het), 7.15 (d, 4 H, H 2 and H 6-*p*-N*Me*$_2$C$_6$H$_4$), 7.0–7.8 (m, H 4-H 7-Het).

(1-Methyl-2-indolyl)bis(4-dimethylaminophenyl)methane (**6**)

M.p. 145–146 °C (EtOH/H_2O). IR (KBr) ν: 1610, 1520, 1350, 820 cm^{-1}. ^{1}H-NMR: δ = 2.90 (s, 12 H, NMe_2), 3.50 (s, 3 H, NMe), 5.45 (s, 1 H, CH), 5.95 (s, 1 H, H 3-Het), 6.70 (d, 4 H, H 3 and H 5-p-N$Me_2$$C_6H_4$), 7.1–7.6 (m, h 4-H 7-Het), 7.10 (d, H 2 and H 6-p-N$Me_2$$C_6H_4$).

Bis(2-benzothienyl)(4-dimethylaminophenyl)methane (**7**)

M.p. 166–168 °C (Me_2CO/H_2O). IR (KBr) ν: 1610, 1520, 1360, 810, 745 cm^{-1}. ^{1}H-NMR: δ = 2.95 (s, 6 H, NMe_2), 5.90 (s, 1 H, CH), 6.70 (d, 2 H, H 3 and H 5-p-N$Me_2$$C_6H_4$), 7.10 (s, 2 H, H 3-Het), 7.25 (d, H 2 and H 6-p-N$Me_2$$C_6H_4$), 7.2–7.9 (m, H 4-H 7-Het). Anal. calcd. for $C_{25}H_{21}NS_2$: C 75.14, H 5.29, N 3.50. Found: C 75.01, H 5.13, N 3.78.

Tris(2-benzothienyl)methane (**8**)

M.p. 133–134 °C (EtOH/H_2). IR (KBr) ν: 1430, 1300, 830, 735 cm^{-1}. ^{1}H-NMR: δ = 6.20 (s, 4 H, H 3-Het and CH); 7.1–7.9 (m, 12 H, H 4-H 7-Het). Anal. calcd. for $C_{25}H_{16}S_3$: C 72.27, H 3.90. Found: 72.67, H 4.13.

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