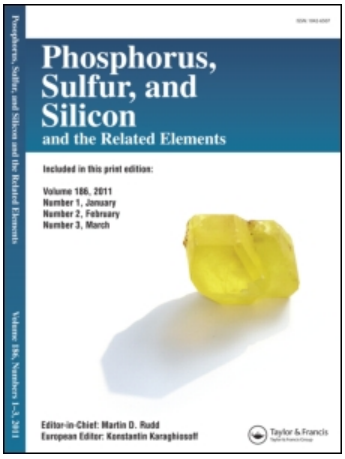

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SYNTHESIS WITH α-HETEROSUBSTITUTED PHOSPHONATE CARBANIONS. XVII.[1] PREPARATION OF DIACYLATED AROMATICS

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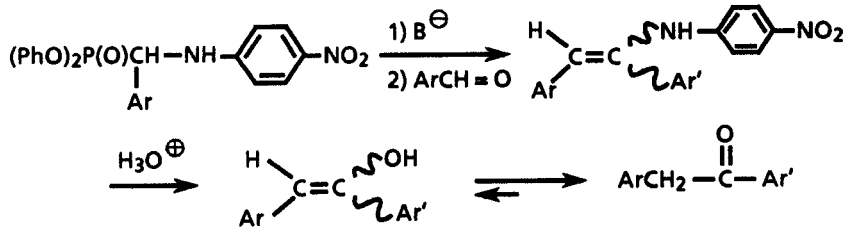
Dianions derived from tetraphenyl arylene-bis-[(4-nitrophenylamino)methyl]-bis-phosphonates react with aromatic and heteroaromatic aldehydes to yield bis-acylated aromatics.

Key words: α-Heterosubstituted phosphonate carbanions; diacylated aromatics; diacylated heteroaromatics; deoxybenzoins, enamines.

INTRODUCTION

In a series of papers we showed that anions derived from diphenyl 1-aryl-1-(4-nitrophenylamino)-phosphonates react with aromatic aldehydes in a convenient way to give via the corresponding enamines, deoxybenzoins[3] (Scheme 1).

A significant advantage of this synthesis of deoxybenzoins over previous methods either by a Grignard reaction[4] or by a Friedel-Crafts reaction[5] is the fact that our method can tolerate practically all types of substituents, whereas the other two procedures are severely restricted as far as substituents are concerned. Thus, the introduction of two acyl groups into aromatic and heteroaromatic rings is generally not possible by a one-step reaction as is possible for the introduction of, e.g. two nitro groups. Therefore, there is only scant information on the synthesis of such compounds. An exception is the synthesis of 1,4-bis-phenacylbenzene which has been prepared by reacting 1,4-dicyanobenzene with benzylmagnesium bromide and subsequent hydrolysis of the Mg-adduct.[6] In the following communication the synthesis of diacylated aromatics as well as a heteroaromatic compound is reported by extending our method of utilizing α-heterosubstituted phosphonate carbanions to include the corresponding dianions.



Scheme 1

RESULTS AND DISCUSSION

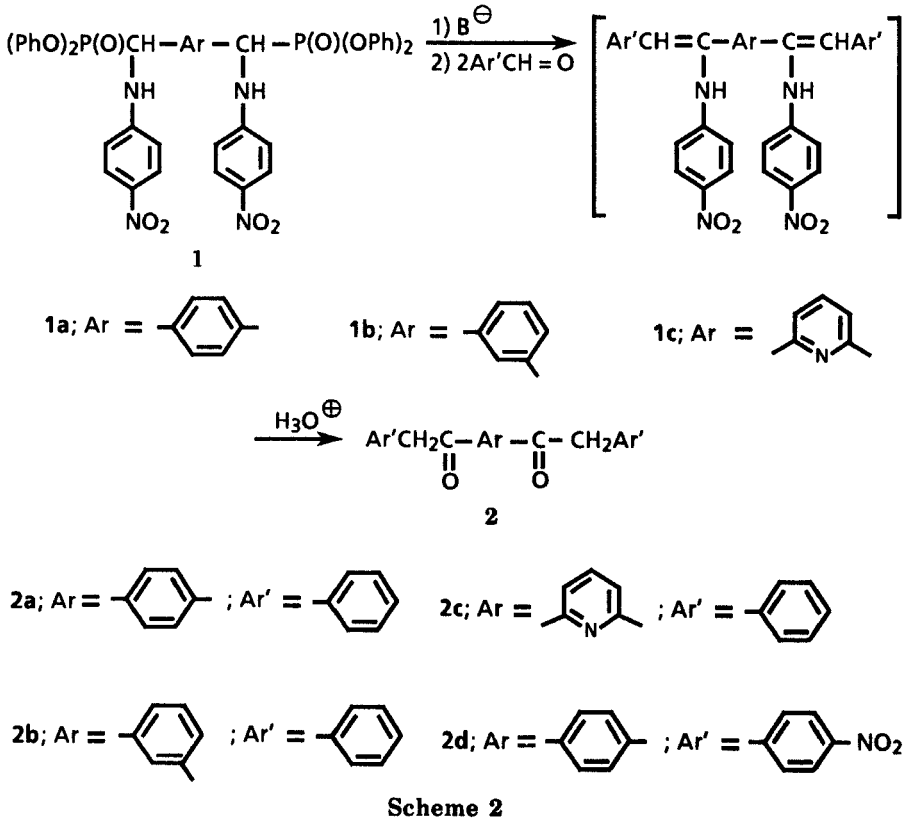
Employing aromatic dialdehydes in the synthesis of the starting phosphonates opens the way via the heterosubstituted phosphonate dianions towards diacylated aromatics according to the following reaction sequence (Scheme 2).

The base used in all reactions was a 10% KOH solution in methanol. The enamines were obtained as oily substances. They were hydrolyzed by using a solution of conc. HCl in methanol without attempts to purify them. The deoxybenzoins were purified either by chromatography or simple recrystallization. Their structural assignments are based on elemental analyses, MS, IR and ^1H NMR spectra. Though the yields of the diacylated aromatics are only average, the method reported here for obtaining such aromatics and heteroaromatics in a simple two-step procedure is remarkable, especially since such species are not easily obtainable by conventional methods.

EXPERIMENTAL

General Procedure for the Preparation of the Bis-phosphonates

The reaction was done in a round-bottom flask equipped with a Dean-Stark trap and a condensor. The dialdehyde and the *p*-nitroaniline were dissolved in 150 mL of benzene and heated to reflux for about



Scheme 2

1 h. Typical amounts used for the reaction were 20 mmol dialdehyde and 40 mmol *p*-nitroaniline. After cooling to room temperature, 40 mmol of diphenyl phosphite were added and the solution refluxed again for about 2 h. A yellow precipate developed. The mixture was allowed to stay overnight at room temperature. The solid was then removed by filtration and the filtrate stored in the refrigerator to induce more precipitation. The crude compound was purified by a short silica gel column (diameter: 10 cm, height: 5 cm). Generally EtOH:$CHCl_3$ = 1:19 was used as solvent. For the final purification the solvent was only partially evaporated and the separated mixture kept below room temperature to precipitate the phosphonate and leave most of the *p*-nitroaniline in solution. A final purification was done by extracting the crystals obtained by chromatography in a Soxhelt apparatus with ethanol. Yields of crude material vary between 50–80%.

Tetraphenyl 1,4-phenylene-bis-[(4-nitrophenylamino)methyl]-bis-phosphonate (**1a**). From terephthaldehyde, *p*-nitroaniline and diphenyl phosphite, yield 48%. m.p. 243–245°C; ^{1}H NMR: 8.0—6.4 (m, 34H), 5.37 (dd, 2H), $J_{P—CH}$ = 24.2 Hz, $J_{P—CH—NH}$ 9.3 Hz; IR (KBr): 3260 cm^{-1} (NH), 1250 cm^{-1} (C—O—P), 1160 cm^{-1} (P=O); MS, m/e: 843 ($M^{+\cdot}$), 826, 705, 609, 593, 471, 375 (base peak), 359. Anal. Calcd. for $C_{44}H_{36}N_4O_{10}P_2$: C, 62.64%; H, 4.30%. Found: C, 62.36%; H, 4.32%.

Tetraphenyl 1,3-phenylene-bis-[(4-nitrophenylamino)methyl]-bis-phosphonate (**1b**). From isophthaldehyde, *p*-nitroaniline and diphenyl phosphite, yield 51%; m.p. 206–208°C; ^{1}H NMR 8.00-6.4 (m, 34H), 5.24 (dd, 2H), $J_{P—C—H}$ 24.9 Hz, $J_{CH—NH}$ 8.6 Hz; IR (KBr) 3280 cm^{-1} (NH), 1200 cm^{-1} (C—O—P), 1175 cm^{-1} (P=O); MS, m/e 843 ($M^{+\cdot}$), 826, 609, 375, 232, 157 (base peak); Anal. Calcd. for $C_{44}H_{36}N_4O_{10}P_2$: C, 62.64; H, 4.30%. Found: C, 62.50%; H, 4.5%.

Tetraphenyl pyridine-2,6-bis-[(4-nitrophenylamino)methyl]-bis-phosphonate (**1c**). From pyridine-2,6-dicarboxaldehyde, *p*-nitroaniline and diphenylphosphite, yield 35%; m.p. 199.5–200°C; ^{1}H NMR 8.1-6.6 (m, 33H); 5.57 (dd, 4H), $J_{P—C—H}$ 21.6 Hz, $J_{P—CH—NH}$ 8.9 Hz; IR (KBr) 3270 cm^{-1} (NH), 1250 cm^{-1} (C—O—P), 1150 cm^{-1} (P=O); MS, m/e 844 ($M^{+\cdot}$), 827, 610 (base peak), 461. Anal. Calcd. for $C_{43}H_{35}N_5O_{10}P_2$: C, 61.21%; H, 4.18%. Found: C, 60.96%; H, 4.37%.

General Procedure for the Preparation of Deoxybenzoins and Hydrolysis of Enamines.

The reactions were carried out in a three-necked flask equipped with a dropping funnel and septa on the other outlets for N_2-protection gas inlet and outlet. The oven-dried glassware was cooled to room temperature under N_2 in a closed system. Generally 2–4 mmol of dried phosphonate were dissolved in ca. 150 mL anhydrous THF and cooled to −78°C by means of a dry ice/isopropanol bath. Potassium hydroxide was used as a 10% methanolic solution. The base solution containing ca. 30 mL THF was used in 1.1 equivalent excess and was added dropwise to the phosphonate solution. The first drop of base changed the color of the solution from clear yellow to orange or red. The addition was completed after about 30 min and the aldehyde was also immediately added slowly in a solution of ca. 30 mL THF through the dropping funnel. The reaction mixture was stirred up to 4 h at −78°C and was allowed to warm to room temperature overnight under N_2 protection. The solvent was evaporated and an orange/red oil was obtained. It was dissolved in 50 mL of methanol and 5 mL HCl (conc.). The mixture was refluxed for about 2 h, the solvent evaporated to dryness, then some water and chloroform were added. The residue was exhaustively extracted with chloroform. The organic phase was then washed several times with water and $NaHCO_3$ solution and was dried over $MgSO_4$. Solvent evaporation yielded a yellow solid. Final purification was done in every case by chromatography on a silica gel column and an appropriate solvent mixture (often $CHCl_3$:EtOH = 19:1). In most cases the compound was recrystallized to obtain an analytically pure sample. Yields vary from 20–28%.

1,4-Diphenacylbenzene, (**2a**). Yield 20%, pale yellow crystals, m.p. 178.5–179.5°C (ethanol-water) (Literature m.p. 180–181°C, Reference 6); ^{1}H NMR 8.04 (s, 4H), 7.28 (s, 10H), 4.28 (s, 4H); IR ($CHCl_3$) 1665 cm^{-1} (C=O); MS, m/e 314 ($M^{+\cdot}$) 223 (base peak), 195, 165, 152, 132, 104, 91, 76. Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05%; H, 5.77%. Found: C, 83.95%; H, 5.94%.

1,3-Diphenacylbenzene (**2b**). Yield 23%, m.p. 81.5–82°C (anhydr. ethanol); ^{1}H NMR 8.62 (dd, 1H), 8.19 (dd, 2H) 7.53 (dd, 1H), 7.28 (s, 10H), 4.29 (s, 4H), J_{meta} 1.6 Hz, J_{ortho} 7.8 Hz; IR ($CHCl_3$) 1665 cm^{-1} (C=O); MS, m/e 314 ($M^{+\cdot}$), 223 (base peak), 165, 152, 104, 91, 76. Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05%; H, 5.77%. Found: C, 84.09%; H, 5.88%.

2,6-Diphenacylpyridine (**2c**). Yield 28%, colorless amorphous solid, m.p. 54.5–55°C, obtained pure by column chromatography on silica gel with CCl_4:$CHCl_3$ solvent system in a ratio of 1:1; ^{1}H NMR 8.21 (d, 2H), 7.9 (dd, 1H), 7.30 (s, 10H) 4.6 (s, 4H), J_{meta} 1.8 Hz, J_{ortho} 7.3 Hz; IR ($CHCl_3$) 1701 cm^{-1} (C=O); MS, m/e 315 ($M^{+\cdot}$) 287, 224, 196, 170 (base peak), 141, 105, 91, 77, 65. Anal. Calcd. for $C_{21}H_{17}NO_2$: C, 79.98%, H, 5.43%, N, 4.44%. Found C, 79.888%, H, 5.44%, N, 4.42%.

1,4-Di-(4-nitrophenacyl)-benzene (**2d**). Yield 27% colorless crystals, m.p. 230–231.5°C (CH_2Cl_2); ^{1}H

NMR 8.2 (d, 4H), 8.1 (s, 4H), 7.4 (d, 4H), 4.4 (s, 4H); IR (CH_2Cl_2), 1700 cm^{-1} (C═O), 1685 cm^{-1} (C═O), 1520 cm^{-1} (NO_2 antisymm. stretch), 1350 cm^{-1} (symm. stretch); MS m/e 375, ($M^{+\cdot}$), 268 (base peak), 238, 165, 132, 120, 106, 91, 76. Anal. Calcd. for $C_{22}H_{16}N_2O_6$: C, 65.35%; H, 3.99%; N, 6.93%. Found: C, 65.44%; H, 4.12%; N, 6.82%.

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