Synthesis of 2-aryl-6-(4-bromophenyl)-4-(2,2-dichlorovinyl)pyridines with the use of 1-aryl-5,5-dichloropenta-2,4-dien-1-ones

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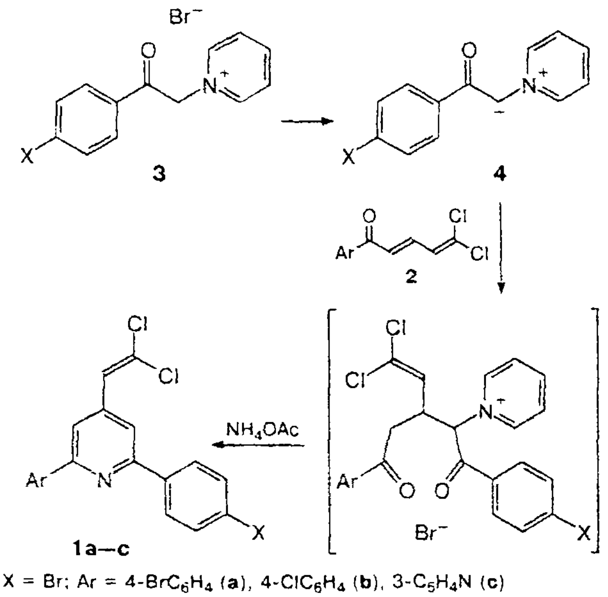
Heating 1-aryl-5,5-dichloropenta-2,4-dien-1-ones with 4-bromophenacylpyridinium bromide in AcOH in the presence of $AcONH_4$ gave 2-aryl-6-(4-bromophenyl)-4-(2,2-dichlorovinyl)pyridines. The reaction products were structurally characterized by ^1H and ^{13}C NMR spectroscopy.

Key words: 1-aryl-5,5-dichloropenta-2,4-dien-1-ones; 2,6-diaryl-4-(2,2-dichlorovinyl)pyridines, synthesis; *N*-phenacylpyridinium salts, cyclization; ^1H and ^{13}C NMR spectra.

Compounds bearing a dihalovinyl group are of interest because this group can further be transformed into, for example, an acetylene (including substituted) fragment.[1] However, the only published way of preparation of 3-(dibromovinyl)pyridines from a corresponding aldehyde is rather complex.[2] In the present work, a one-step method for the synthesis of 4-(dichlorovinyl)pyridines **1** from available 1-aryl-5,5-dichloropenta-2,4-dien-1-ones (**2**) is proposed.

Previously, we obtained a series of carbo- and heterocyclic compounds from 1-aryl-5,5-dichloropenta-2,4-dien-1-ones.[3,4] It was noted that, in many cases, these ketones behave like chalcones. Based on the known procedures for the synthesis of pyridines from chalcones,[5,6] we attempted to obtain some 2,6-diaryl-4-(2,2-dichlorovinyl)pyridines (**1**) from 1-aryl-5,5-dichloropenta-2,4-dien-1-ones (**2**) (Scheme 1).

Scheme 1

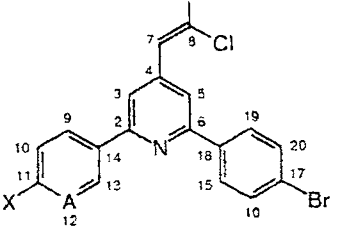


X = Br; Ar = 4-BrC_6H_4 (**a**), 4-ClC_6H_4 (**b**), 3-C_5H_4N (**c**)

Compounds **1** were obtained by heating ketones **2** with pyridinium salts **3** in AcOH in the presence of $AcONH_4$. The reaction occurs at 83—95 °C (in the case of 1-(pyridin-3-yl)-5,5-dichloropenta-2,4-dienone (**2c**), at 105 °C). At a lower temperature, ylide **4** seems not to be generated yet, whereas a further increase in temperature results in complete resinification of the reaction mixture.

In such a way, we could synthesize the target pyridines only from pyridinium salt **3** for X = Br. With salts **3** for X = H or Et, the reaction mixture resinifies already at 80 °C (below this temperature, the reaction is not initiated); in the case of X = NO_2, no reaction occurs even at the boiling point of AcOH. Presumably, the presence of a halogen atom in the benzene ring largely stabilizes the intermediate ylide **4**, but does not deactivate it.

The compounds synthesized were structurally characterized by ^1H and ^{13}C NMR spectroscopy (Tables 1 and 2, respectively). The ^1H NMR spectra show singlets at δ 6.90 or 6.97 from the proton of the dichlorovinyl group and singlets at δ 7.72—7.85 corresponding to the pyridine protons. ^{13}C NMR signals were assigned with the use of selective double heteronuclear resonance, as well as considering the multiplicity of signals and the



a: X = Br, A = CH
b: X = Cl, A = CH
c: X = H, A = N

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Table 1. ^1H NMR spectra (δ) for pyridines **1a—c***

Compound	H(3)	H(5)	H(7)	H(15)	H(16)	H(9)	H(10), H(12)	H(11)	H(13)
1a	7.73	7.73	6.90	7.96	7.62	7.96	7.62	—	7.96
1b	7.725	7.72	6.90	7.96	7.62	8.03	7.46	—	8.03
1c	7.85	7.82	6.97	8.00	7.65	8.42	7.45	8.70	9.30

* The observed multiplicity of signals and the corresponding coupling constants correlate with those expected for the proposed structures (*cf.* Refs. 8 and 9).

Table 2. ^{13}C NMR spectra (δ) for pyridines **1a—c**

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
1a	156.4	117.8	142.6	117.8	156.4	126.7	126.0	128.7	132.0
1b	156.4	117.79	142.6	117.85	156.4	126.8	125.9	128.3	128.6
1c	155.1	118.3	142.9	118.1	156.8	126.6	126.3	134.5	123.7

Compound	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
1a	124.0	132.0	128.7	137.7	128.7	132.0	124.0	137.7
1b	135.6	128.6	128.3	137.3	129.0	132.0	124.0	137.8
1c	150.4	—	148.5	134.5	128.6	132.1	124.1	137.6

influence of the substituents on the ^{13}C chemical shifts for monosubstituted benzenes.[7]

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AC 200P (200 and 50.3 MHz, respectively) and Bruker AM 300 instruments (300 and 75.47 MHz, respectively) in DMSO-d_6. The signals of the CH groups were distinguished from those of the quaternary C atoms using the standard JMOD HX.AU procedure.

Melting points were determined on a Boetius stage and are given uncorrected. The course of the reactions was monitored by TLC on Silufol UV-254 plates in hexane—AcOEt (3 : 1 to 1 : 1 by volume) as an eluent.

1-Aryl-5,5-dichloropenta-2,4-dien-1-ones (2a,b) were prepared according to the known procedures.[10,11]

5,5-Dichloro-1-(pyridin-3-yl)penta-2,4-dien-1-one (2c) was obtained as described earlier[11] from 3-acetylpyridine and 3.3-dichloroacrolein. Yield 68%, m.p. 140—141 °C. Found (%): C, 52.60; H, 3.14; Cl, 30.97; N, 5.62. $C_{10}H_7Cl_2NO$. Calculated (%): C, 52.66; H, 3.09; Cl, 31.09; N, 6.14.

2-Aryl-6-(4-bromophenyl)-4-(2,2-dichlorovinyl)pyridines (1a—c). A solution of dienone **2** (5 mmol), pyridinium salt **3** (5 mmol), and $AcONH_4$ (30 mmol) in 8 mL of AcOH was heated to 83—90 °C (in the case of 3-pyridinyldienone, to 105 °C) and kept at this temperature for 4—5 h (monitoring by TLC). The reaction mixture was cooled to −20 °C and poured into water (20 mL). The resulting solution was alkalized with Na_2CO_3 to pH 7.5 and left at −4 °C for 16 h. The precipitate that formed was filtered off, dried, and recrystallized from aqueous EtOH.

2,6-Di(4-bromophenyl)-4-(2,2-dichlorovinyl)pyridine (1a). Yield 61%, m.p. 126—127 °C. Found (%): C, 47.67; H, 2.46; Br, 32.74; Cl, 14.21; N, 2.73. $C_{19}H_{11}Br_2Cl_2N$. Calculated (%): C, 47.15; H, 2.29; Br, 33.02; Cl, 14.65; N, 2.89.

2-(4-Bromophenyl)-6-(4-chlorophenyl)-4-(2,2-dichlorovinyl)pyridine (1b). Yield 64%, m.p. 142—143 °C. Found (%): C, 52.02; H, 2.73; Br, 17.88; Cl, 24.04; N, 3.43. $C_{19}H_{11}BrCl_3N$. Calculated (%): C, 51.92; H, 2.52; Br, 18.18; Cl, 24.20; N, 3.19.

6-(4-Bromophenyl)-4-(2,2-dichlorovinyl)-2-(pyridin-3-yl)-pyridine (1c). Yield 55%, m.p. 134—135 °C. Found (%): C, 54.55; H, 2.88; Br, 19.21; Cl, 17.45; N, 6.79. $C_{18}H_{11}BrCl_2N_2$. Calculated (%): C, 53.24; H, 2.73; Br, 19.68; Cl, 17.46; N, 6.90.

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