Brief Communications

New aromatizational transformations of 4-methyl-4-trichloromethyl-substituted 2,5-cyclohexadiene triphenylphosphonium and pyridinium ylides: abstraction or 1,6-migration of the CCl_3 group

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4-Methyl-4-trichloromethylcyclohexadiene triphenylphosphonium ylide obtained by treatment of (1-methyl-1-trichloromethylcyclohexa-2,4-dien-4-yl)-triphenylphosphonium bromide with Bu^nLi in THF is stabilized by the abstraction of the CCl_3 group to give (*p*-tolyl)triphenylphosphonium cation, which was isolated as the corresponding hydroxide. Conversely, an analogous pyridinium ylide, obtained by treatment of *Z*/*E* stereoizomeric *N*-(1-methyl-1-trichloromethylcyclohexa-2,5-dien-4-yl)pyridinium bromide with a base (piperidine in CD_2Cl_2, Bu^nLi in THF), at temperatures above −40 °C, undergoes a novel high-yield aromatizational skeletal rearrangement with migration of the CCl_3 group to position 2 of the heterocycle.

Key words: phosphonium salts, phosphonium ylides, pyridinium salts, pyridinium ylides, 1,2-dihydropyridines, rearrangements, migrations.

In our studies of transformations of *para*-semiquinoid ligands and their derivatives containing Group V elements,[1] we prepared 4-methyl-4-trichloromethylcyclohexa-2,5-diene ylides of nitrogen and phosphorus onium derivatives. Previously it has been found[2] that a compound of this type, triphenylphosphonium ylide (**1**), which is formed as an intermediate upon deprotonation of the corresponding 1,4-cyclohexadienyl phosphonium salts by nitrogen-containing bases, is extremely reactive and easily undergoes self-protonation at the instant of proton abstraction thus giving the rearranged 1,3-cyclohexadienylphosphonium salt (**2**). In the present study dealing with the behavior of the compounds in question in more basic aprotic media (BuLi in THF), we were able to obtain the expected ylide **1** in solution, as indicated by the intense red-orange coloration of the reaction solution at −80 °C. Heating the mixture to −20 °C followed by isolation in air of the precipitate formed gave triphenyl(*p*-tolyl)phosphonium hydroxide (**3**) in a high yield. This attests that the intermediate ylide can undergo aromatization through elimination of the CCl_3 group from the geminal unit of the molecule (Scheme 1).

A similar pyridinium ylide (**4a**) derived from a stereoisomeric mixture of *N*-(4-methyl-4-trichloromethyl-2,5-cyclohexadienyl)pyridinium bromides (**5a**), prepared by treatment of the corresponding *E*/*Z*-isomeric bromides **6** with excess pyridine in benzene, undergoes a

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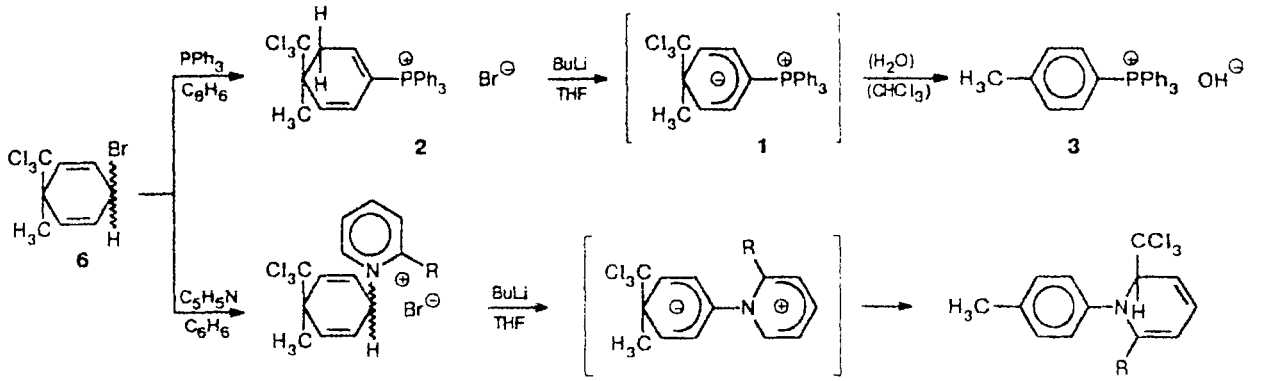
Scheme 1



different type of transformation under the conditions studied. Treatment of salt **5a** in THF with a hexane solution of BuLi at −80 °C results in an intense blue-violet color, which gradually disappears when the solution is slowly warmed to ~20 °C. *N*-(*p*-Tolyl)-2-trichloromethyl-1,2-dihydropyridine (**7a**) resulting from 1,6-migration of the CCl_3 group from the semiquinoid ring to the pyridine ring was isolated in 76.2% yield by column chromatography of the reaction mixture. Treatment of salt **5a** with weaker bases (piperidine in CD_2Cl_2 at −80 °C in an NMR tube) also yields compound **7a**, together with a new product (25% with respect to **7a**, judging by integral intensities of the signals). According to evaluation of increments of the chemical shifts, its structure corresponds to *N*-(*p*-tolyl)pyridinium cation. The fact that the use of both bases leads only to the 2-substituted 1,2-dihydropyridine but gives no 4-substituted 1,4-isomer can serve as evidence of an intramolecular mechanism of the observed rearrangement of ylide **4a**. Nevertheless, the possibility of these reactions occurring by an intermolecular mechanism, for example as cross-alkylation, also cannot be ruled out. It is of interest that when a substituent is introduced into one of the α-positions of the initial pyridinium salt **5b**, dihydropyridine **7b** with the CCl_3 group located at the nonsubstituted carbon atom of the heterocyclic ring is obtained as the only product of the rearrangement of the corresponding ylide **4b**.

Experimental

The course of the reactions was monitored by TLC on Silufol-UV 254 plates; the plates were visualized by UV-irradiation. NMR spectra were recorded on a Bruker AMX 400 spectrometer (operating at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C). 1-Methyl-1-trichloromethylcyclohexa-2,5-dien-4-ol was prepared by a known procedure.[3] Pyridine and 2-picoline were distilled over KOH. The solvents were dried by standard procedures.

***E/Z*-4-Bromo-1-methyl-1-trichloromethylcyclohexa-2,5-diene (6).** One drop of C_5H_5N and then, over a period of 30 min, a solution of PBr_3 (0.666 g, 25 mmol) in 5 mL of anhydrous CCl_4 were added to a solution of *E/Z*-isomers of 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-ol (1.678 g, 74 mmol) in 25 mL of anhydrous CCl_4. The mixture was stirred for 2 h, then washed with a 5% solution of K_2CO_3 (20 mL) and with H_2O (2×20 mL), and dried with Na_2SO_4. Evaporation of the solvent *in vacuo* gave 2.067 g (96.6%) of bromide **6**. Found (%): C, 33.41; H, 2.78. $C_8H_8BrCl_3$. Calculated (%): C, 33.09; H, 2.70. *E*-isomer. ^1H NMR ($CDCl_3$), δ: 1.62 (s, 3 H, Me); 5.22 (tt, 1 H, CHBr, ^3J = 3.8 Hz, ^4J = 0.9 Hz); 6.18 (dd, 2 H, CH, ^3J = 10.4 Hz, ^4J = 0.9 Hz); 6.28 (dd, 2 H, CH, ^3J = 10.4 Hz, ^4J = 3.8 Hz). ^{13}C NMR ($CDCl_3$),: 23.27 (Me); 41.67 (CHBr); 53.21 (CMe.); 106.89 (CCl_3); 129.24 (CH); 131.06 (CH). *Z*-isomer. ^1H NMR ($CDCl_3$): 1.75 (s, 3 H, Me); 5.22 (tt, 1 H, CHBr, ^3J = 4.0 Hz, ^4J = 1.0 Hz); 6.15 (dd, 2 H, CH, ^3J = 10.6 Hz, ^4J = 1.0 Hz); 6.24 (dd, 2 H, CH, ^3J = 10.6 Hz, ^4J = 4.0 Hz). ^{13}C NMR ($CDCl_3$),: 25.66 (Me); 41.17 (CHBr); 53.48 (CMe); 106.89 (CCl_3); 128.67 (CH); 131.48 (CH).

***N*-(4-Methyl-4-trichloromethylcyclohexa-2,5-dienyl)pyridinium bromide (5a).** Pyridine (474 mg, 6 mmol) was added to a solution of bromide **6** (581 mg, 2 mmol) in 15 mL of benzene. The mixture was kept for 2 days at ~20 °C, and the resulting white crystalline precipitate was filtered off, washed with C_6H_6 (5×5 mL), and dried to give 583 mg (78.9%) of pyridinium salt **5a**. Found (%): C, 42.55; H, 3.69; N, 3.79. $C_{13}H_{13}BrCl_3N$. Calculated (%): C, 42.26; H, 3.55; N, 3.79. ^1H NMR ($CDCl_3$), δ: 1.58 (s, 3 H, Me); 6.32 (dd, 2 H, CH olef., ^3J = 10.3 Hz, 3.3 Hz); 6.54 (dd, 2 H, CH olef., ^3J = 10.3 Hz, ^4J = 1.8 Hz); 6.86 (tt, 1 H, CH, ^3J = 3.3 Hz, ^4J = 1.8 Hz); 8.20 (dd, 2 H, *m*-CH het., ^3J = 7.8 Hz, 6.8 Hz); 8.61 (tt, 1 H, *p*-CH het., ^3J = 7.8 Hz, ^4J = 1.3 Hz); 9.52 (dd, 2 H, *o*-CH het., ^3J = 6.8 Hz, ^4J = 1.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 25.30 (Me); 53.50 (CMe); 64.60 (CH aliph.); 105.50 (CCl_3); 124.59 (CH olef.); 128.88 (*m*-CH het.); 134.74 (CH olef.); 144.14 (*o*-CH het.); 146.34 (*p*-CH het.).

2-Methyl-*N*-(4-methyl-4-trichloromethylcyclohexa-2,5-dienyl)pyridinium bromide (5b). 2-Picoline (158 mg, 1.68 mmol) was added to a solution of bromide **6** (164 mg, 0.56 mmol) in 2 mL of benzene. The mixture was kept for 2 days at ~20 °C, and then the white finely crystalline precipitate was filtered off, washed with C_6H_6 (3×2 mL), and dried to give 90.8 mg (42.3%) of product **5b**. Found (%): C, 43.89; H, 4.01; N, 3.56. $C_{14}H_{15}BrCl_3N$. Calculated (%): C, 43.84; H, 3.94; N, 3.65. ^1H NMR ($CDCl_3$), δ: 1.62 (s, 3 H, Me);

3.36 (s, 3 H, Me het.); 6.44 (dd, 2 H, CH olef., ^3J = 10.4 Hz, ^4J = 3.1 Hz); 6.54 (m, 1 H, CH aliph.); 6.60 (dd, 2 H, CH olef., ^3J = 10.4 Hz, ^4J = 2.0 Hz); 7.87 (m, 1 H, CH het.); 8.13 (m, 1 H, CH het.); 8.41 (m, 1 H, CH het.); 8.71 (m, 1 H, CH het.).

***N*-(*p*-Tolyl)-2-trichloromethyl-1,2-dihydropyridine (7a).** An equimolar amount of a 0.85 *M* solution of BuLi in hexane was added at −78 °C to a suspension of *N*-(4-methyl-4-trichloromethylcyclohexa-2,5-dienyl)pyridinium bromide (73.9 mg, 0.2 mmol) in 16 mL of anhydrous THF. The mixture acquired a violet color. It was stirred for 30 min at −78 °C and then warmed to ~20 °C over a period of 2 h. As the mixture warmed, its color gradually changed to yellow. The solvent was evaporated *in vacuo*, and the residue was chromatographed on a column (silica gel 40/100, $CHCl_3$). Evaporation of the solvent gave 44 mg (76.2%) of dihydropyridine **7a** as a pale yellow oil. ^{1}H NMR ($CDCl_3$), δ: 2.33 (s, 3 H, Me); 5.38 (ddd, 1 H, CH het., ^3J = 7.6 Hz, 5.7 Hz, ^4J = 1.3 Hz); 5.40 (d, 1 H, CH het., ^3J = 5.6 Hz); 5.69 (dddd, 1 H, CH het., ^3J = 9.6 Hz, 5.7 Hz, ^4J = 1.3 Hz, 1.0 Hz); 6.47 (dd, 1 H, CH het., ^3J = 9.6 Hz, 5.6 Hz); 6.71 (dd, 1 H, CH het., ^3J = 7.6 Hz, ^4J = 1.0 Hz); 7.16 (d, 2 H, CH arom., ^3J = 8.9 Hz); 7.22 (d, 2 H, CH arom., ^3J = 8.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.83 (Me); 72.44 (CH het.); 102.29 (CH het.); 105.37 (CCl_3); 109.95 (CH het.); 121.46 (CH arom.); 127.90 (CH het.); 130.00 (CH arom.); 133.46 (C arom.); 133.85 (CH het.); 145.85 (C arom.).

6-Methyl-*N*-(*p*-tolyl)-2-trichloromethyl-1,2-dihydropyridine (7b). An equimolar amount of C_5H_5N was added at −70 °C to a solution of pyridinium salt **5b** (51.4 mg, 0.134 mmol) in 1 mL of $CHCl_3$. The violet mixture was warmed up to ~20 °C over a period of 1 h (during this period, the color changed to yellow) and chromatographed on a column (silica gel 40/100, $CHCl_3$) to give 13.5 mg (33.3 %) of **7b** as a pale yellow oil. ^{1}H NMR ($CDCl_3$), δ: 2.29 (s, 3 H, Me arom.); 2.60 (s, 3 H, Me het.); 4.73 (d, 1 H, CH het., ^3J = 6.4 Hz); 5.37 (m, 1 H, CH het.); 5.53 (dd, 1 H, CH het., ^3J = 9.3 Hz, 6.4 Hz); 6.36 (dd, 1 H, CH het., ^3J = 9.3 Hz, 5.7 Hz); 7.09 (br.d. 1 H, CH tol., ^3J = 7.9 Hz); 7.21 (d, 1 H, CH arom., ^3J = 7.9 Hz).

The reaction of phosphonium salt 2 with BuLi. An equimolar amount of a 0.85 *M* solution of BuLi was added at −80 °C to a suspension of salt **2** (80.5 mg, 0.146 mmol) in 5 mL of anhydrous THF. The color of the reaction mixture immediately changed to red-orange. The mixture was stirred for 30 min at −80 °C, then warmed to ~20 °C over a period of 2 h. The light gray precipitate that formed was separated by centrifugation, washed with 2 mL of THF, and dissolved in 5 mL of CH_2Cl_2, and the solution was filtered. The solvent was evaporated *in vacuo* to give 37 mg (68.6%) of **3** as an almost colorless thick oil, which slowly crystallized in a refrigerator. ^{1}H NMR ($CDCl_3$), δ: 2.09 (br.s, 1 H, OH); 2.50 (s, 3 H, Me); 7.46 (dd, 2 H, CH arom., $^3J_{P-H}$ = 12.7 Hz, $^3J_{H-H}$ = 8.3 Hz); 7.52–7.61 (m, 8 H, CH arom.); 7.76 (m, 6 H, CH arom.); 7.87 (m, 3 H, CH arom.).

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