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Novel 1,2-Phenyl Shift in Silver-assisted Reaction of Triphenylchloroallene with Aromatic Amines

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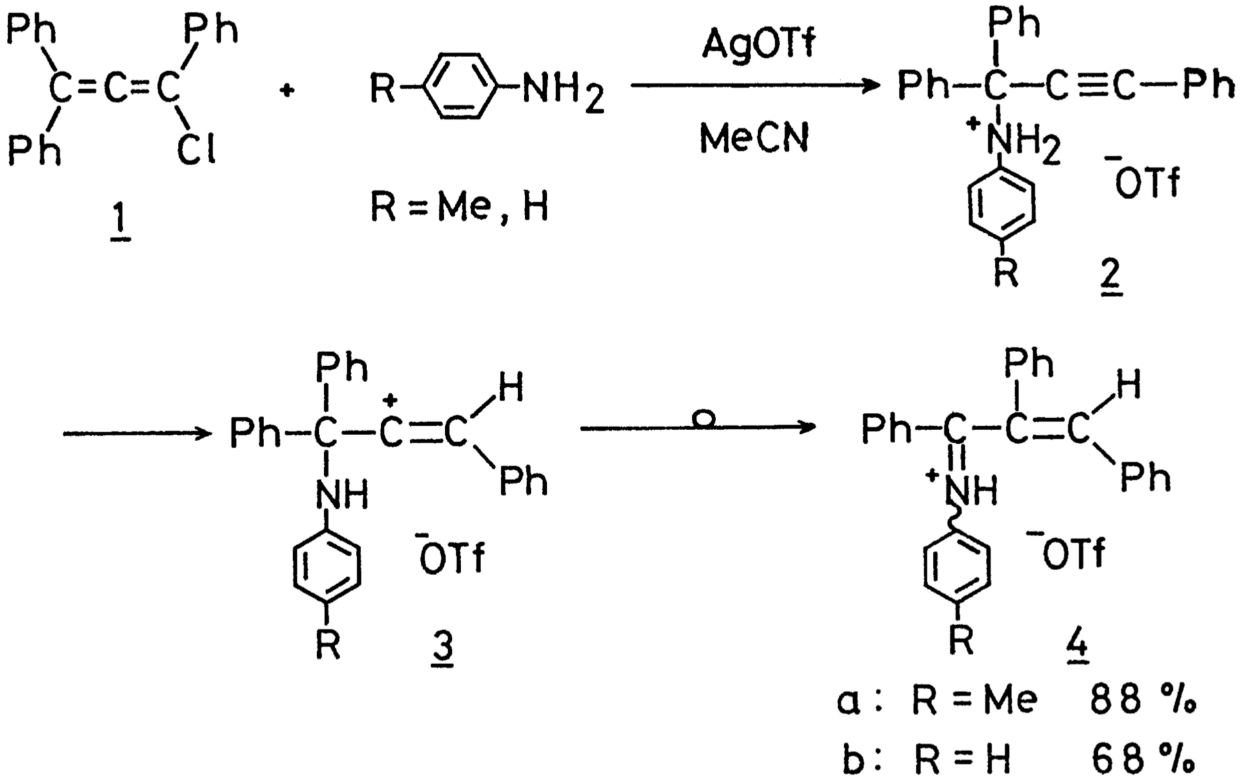
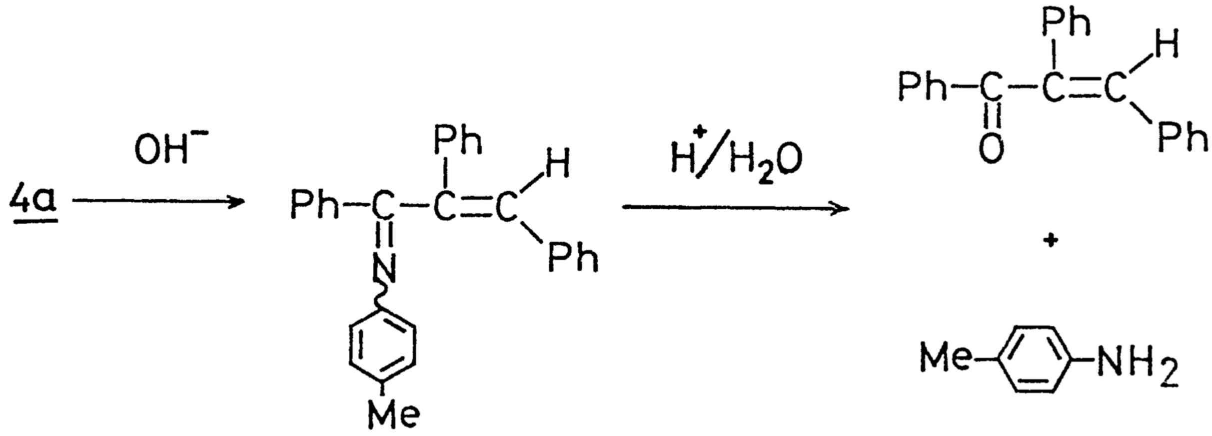
Triphenylchloroallene reacted with aromatic amines in the presence of silver triflate to give 2,3,4-triphenyl-1-aza-1,3-butadiene derivatives via a novel 1,2-phenyl shift.

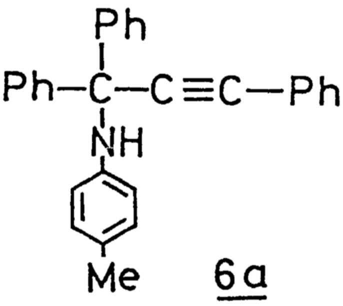
1,2-Aryl shift has been observed in many types of carbocations, carbenes, and nitrenes.[1)] Although it has been established by Schiavelli and coworkers that allenyl cations generated by solvolysis of the corresponding allenyl chlorides react with nucleophiles at the propargyl position in the absence of a bulky substituent on the position, no rearrangement has been observed in those cases.[2)] Herein we report a novel 1,2-phenyl shift in the reaction of triphenylchloroallene with silver triflate and aromatic amines.

A solution of triphenylchloroallene 1 (2 mmol), p-toluidine (2.4 mmol), and silver triflate (2 mmol) in acetonitrile (10 ml) was stirred for 11 h at room temperature. After filtration of silver chloride, evaporation of the solvent gave crystals, mp 225-227 °C (MeCN-ether). The crystals were identified by their chemical transformation and spectral data[3)] to iminium triflate 4a (88%). Treatment of 4a (500 mg) with a mixed solvent of 2 M NaOH aqueous solution, ether, and benzene gave 1-(p-methylphenyl)-2,3,4,-triphenyl-1-azabuta-1,3-diene 5a,[4)] quantitatively, mp 175-176 °C (EtOH-benzene). Acid hydrolysis of 5a with 2.5 M HCl aqueous EtOH solution (reflux, 1 h) gave benzoyl-trans-stilbene, mp 84-86 °C (lit.,[5)] 88-89 °C) and p-toluidine. Similar reaction of 1 with aniline and silver triflate afforded the corresponding iminium triflate 4b,[3)] mp 205-208 °C. The products, 4a and 4b, obtained from the silver-assisted reaction of triphenylchloroallene 1 with aromatic amines bear a phenyl-migrated skeleton. Then, factors affecting the 1,2-phenyl migration have been examined.

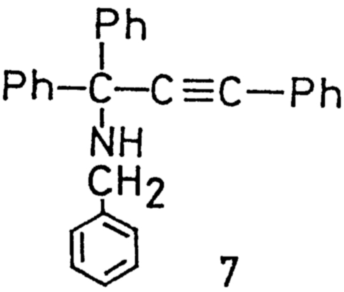
Presence of potassium carbonate during the reaction of 1 with silver triflate and p-toluidine resulted in the formation of a new product, propargyl tolylamine 6a4) (21%), mp 114-116 °C (EtOH), in addition to 5a (67%). This suggests that potassium carbonate has partly prevented the 1,2-phenyl migration and protonated amine 2 is an intermediate. In fact, the treatment of amine 6a with 70% perchloric acid in acetonitrile followed by the treatment with sodium hydroxide afforded 1-azabuta-1,3-diene 5a quantitatively. In contrast to the cases of p-toluidine and aniline, benzylamine did not induce the 1,2-phenyl migration but afforded propargyl benzylamine 74) (53%). Therefore, the 1,2-phenyl migration in the silver-assisted reaction is strongly dependent on the basicity of amines used. To cause the 1,2-phenyl migration the resulting propargyl ammonium triflate 2 must transfer proton from the nitrogen atom to







6a



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the acetylenic carbon.[6)] The 1,2-migration of phenyl group is surely accelerated by the α nitrogen in a similar manner to pinacol rearrangements.[7)]

References

1) Reviews: J. March, "Advanced Organic Chemistry," 2nd ed, McGraw-Hill, New York (1972); "Rearrangements in Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 1; T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry," 3rd ed, Harper & Row, New York (1987).

2) P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, "Vinyl Cations," Academic Press, New York (1979), pp. 246-270 and references cited therein.

3) 4a: ^{1}H NMR (CD_3CN) δ 2.40 (s, Me), 6.83-7.78 (m, ArH); Calcd for $C_{29}H_{24}O_3F_3NS$: C, 66.53; 4.62; N, 2.68%. Found: C, 66.52; H, 4.64; N, 2.66%. 4b: Calcd for $C_{28}H_{22}O_3F_3NS$: C, 66.00; H, 4.35; N, 2.75%. Found:

C, 65.78; H, 4.34; N, 2.75%.

4) 5a: ^{1}H NMR ($CDCl_3$) δ 2.23 (s, Me), 6.54-7.85 (m, ArH); ^{13}C NMR ($CDCl_3$) δ 20.90 (Me), 120.95, 123.53, 127.88, 128.07, 128.37, 128.52, 129.20, 129.93, 133.25, 139.26, 139.45, 141.84, 148.73, 149.31, 165.87 (C=N). 6a: ^{1}H NMR ($CDCl_3$) δ 2.17 (s, Me), 4.08 (s, NH), 6.33-7.70 (m, ArH); Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75%. Found: C, 89.73; H, 6.16; N, 3.72%. 7: Oil; ^{1}H NMR (CCl_4) δ 1.88 (s, NH), 3.86 (s, CH_2), 7.06-8.20 (m, ArH); IR 3300 cm^{-1} (NH).

5) W. B. Black and R. E. Lutz, J. Am. Chem. Soc., 75, 5900 (1953).

6) J. J. Janas, E. T. Asirvatham, and E. McNelis, Tetrahedron Lett., 26, 1967 (1985); K. Vittinghoff and K. Griesbaum, ibid., 22, 1889 (1981).

7) Y. Pocker, "Molecular Rearrangements," ed by P. de Mayo, Interscience Publishers, New York (1963), Chap. 1; C. J. Collins and J. F. Eastham, "The Chemistry of the Carbonyl Group," ed by S. Patai, Interscience Publishers, New York (1966), Chap. 15.

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