Direct C≡C Triple Bond Formation from the C=C Double Bond with Potassium *tert*-Butoxide in Dimethylformamide containing Trace Amounts of Oxygen

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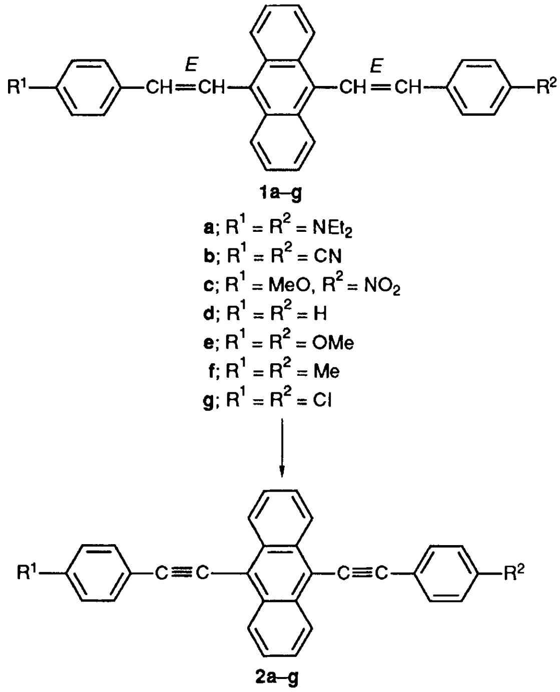
A novel and facile method for direct acetylenic bond formation from the C=C double bond by treatment with KOBu^t in dimethylformamide has been found both in a 9,10-bis(4'-substituted styryl)anthracene series and in a 4-substituted 4'-nitro-stilbene series; its scope and limitations have been examined.

The development of methods of formation of the C≡C triple bond in organic structures has been amply reviewed in recent years.[1] The classical method of formation of the acetylenic bond is elimination of a stable substance from a more saturated structure. In the past the major elimination route has involved the removal of hydrogen halide molecules, *i.e.* dehydrohalogenation.

In this paper, we report a novel and facile method for direct acetylenic bond formation by dehydrogenation from the C=C double bond by treatment with KOBu^t in dimethylformamide (DMF) containing orginally trace amounts of molecular oxygen.[2] We have applied this method to the synthesis of two series of compounds (*i*) 9,10-bis(4'-substituted phenylethynyl)anthracenes and (*ii*) 4-substituted 4'-nitro-diphenylacetylenes.

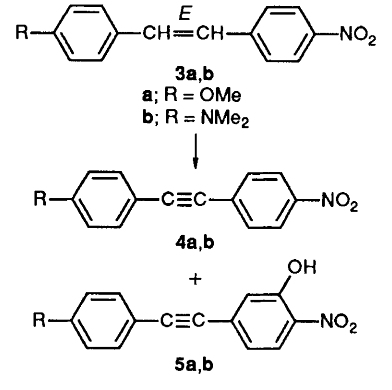
The series of compounds (*i*) are particularly interesting in the field of peroxyoxalate chemiluminescence as an enhancer.[3] In the course of the systematic preparation of the



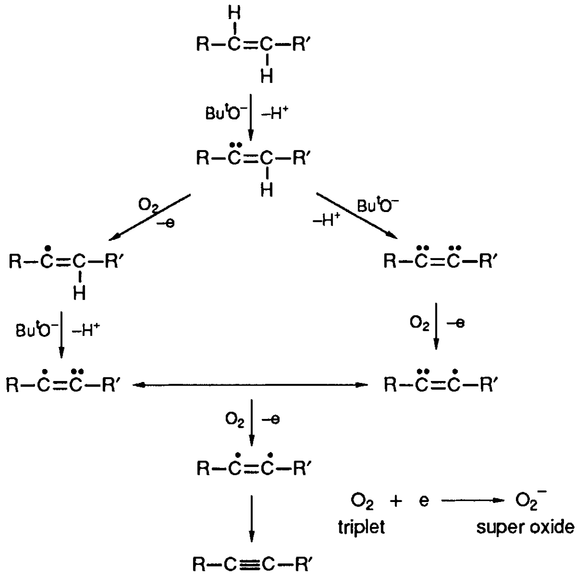
Scheme 1

compound 2, we have found that the acetylenes **2a–c**† were obtained at room temperature from the corresponding alkene **1a–c**[4] by treatment with a large excess of KOBu^t in DMF dried over a molecular sieve.

A typical procedure for the preparation of **2a** is as follows; a mixture of the alkene (**1a**, 0.09 g, 0.20 mmol) and KOBu^t (0.34 g, 3.04 mmol) in DMF (150 cm^3) was stirred for 5 min at room temperature and then poured into water (300 cm^3). The mixture was extracted with CH_2Cl_2 (100 cm^3 × 2), washed with HCl (2 mol dm^{-3}, 50 cm^3) and dried over $MgSO_4$. Evaporation of the extract resulted in dark-orange crystals and these were recrystallised from CH_2Cl_2 to give pure compound **2a**.† Other bases (NaH, NaOEt, NaOMe, Et_3N and KOH) and solvents (DMSO, THF, benzene and EtOH) were used to check whether the reaction takes place or not; it was found that the combination of KOBu^t and DMF or DMSO was essential. Interestingly, the reaction did not occur almost at all in DMF degassed with nitrogen, but after that, proceeded smoothly by bubbling oxygen into the above mixture. Consequently, oxygen participates essentially in the triple bond formation. These acetylenes could not be prepared by the classical method because a bromination reaction did not proceed to the corresponding alkenes. However, the acetylenes **2d–g**[5] which can be easily prepared by the classical method (dehydrobromination of the bromo-adduct of the alkene **1**), could not be obtained at all by the new method.



Scheme 2



Scheme 3

Accordingly, the electronic character of substituents on the benzene rings seems to have a very large effect on the reaction.

Diphenylacetylenes bearing an electron-donor on one end and an electron-acceptor on the other end of the molecule have a potential application to non-linear optics[6] together with the corresponding stilbenes. The one-step synthesis of diphenylacetylenes **4a,b**† from stilbenes **3a,b** was successfully carried out under similar reaction conditions (**3**:KOBu^t = 1:4) as in (*i*). Moreover, we found unexpectedly that the use of a large excess of KOBu^t gave the hydroxy compounds **5a,b**.†

A solution of the stilbene **3a** (0.20 g, 0.78 nmol) and KOBu^t (1.32 g, 0.12 mmol) in DMF (50 cm^3) was stirred for 90 min at room temperature. The reaction mixture was poured into water (200 cm^3) and mixed with HCl (2 mol dm^{-3}, 30 cm^3). The organic layer was extracted with benzene (100 cm^3 × 2) and was washed with NaOH (2 mol dm^{-3}, 60 cm^3).‡ The alkaline water layer was neutralised with HCl, extracted with benzene (50 cm^3 × 4) and the benzene layer dried with $MgSO_4$. Evaporation of the extract resulted in brownish-yellow crystals which were recrystallised from EtOH to give pure compound **5a**.†

The reaction mechanisms of both the oxidative dehydrogenation of the CH=CH bond to the triple bond and of the succeeding hydroxylation§ into the *ortho*-position of a nitro

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† *Selected spectroscopic data:* **2a**: Yield 67%; m.p. 263–265 °C; IR ν_{max}/cm^{-1} 2200; EI-MS (*m/z*) 453 (M$^+$). **2b**: Yield 28%; m.p. 258–260 °C; IR ν_{max}/cm^{-1} 2200, EI-MS (*m/z*) 520 (M$^+$). **2c**: Yield 18%; m.p. 324–325 °C; IR ν_{max}/cm^{-1} 2240, 2210, EI-MS (*m/z*) 428 (M$^+$). **4a**: Yield 39%; m.p. 118–120 °C (lit. 122–123 °C);[7] IR ν_{max}/cm^{-1} 2200 EI-MS (*m/z*) 253 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3H, MeO), 6.91 (d, 2H, *J* 8.8 Hz), 7.50 (d, 2H, 8.8), 7.63 (d, 2H, 8.8) and 8.20 (d, 2H, 8.8). **4b**: Yield 39%; m.p. 207–211 °C (lit. 214–217 °C);[8] IR ν_{max}/cm^{-1} 2210; EI-MS (*m/z*) 266 (M$^+$); ^{1}H NMR 3.02 (s, 6H, Me_2N), 6.67 (d, 2H, 7.0), 7.43 (d, 2H, 7.0), 7.59 (d, 2H, 8.9) and 8.18 (d, 2H, 8.9). **5a**: Yield 43%; m.p. 163–166 °C; IR ν_{max}/cm^{-1} 2220; EI-MS (*m/z*) 269 (M$^+$); ^{1}H NMR 3.85 (s, 3H, MeO), 6.91 (d, 2H, 9.5), 7.07 (dd, 2H, 8.8, 1.8), 7.26 (d, 1H, 1.8), 7.49 (d, 2H, 9.5), 8.07 (d, 1H, 8.8) and 10.64 (s, 1H, OH). **5b**: Yield 53%; m.p. 197–200 °C; IR ν_{max}/cm^{-1} 2200; EI-MS (*m/z*) 282 (M$^+$); ^{1}H NMR 3.02 (s, 6H, Me_2N), 6.66 (d, 2H, 8.8), 7.04 (dd, 2H, 8.8, 1.8), 7.21 (d, 1H, 1.8), 7.42 (d, 2H, 8.8), 8.03 (d, 1H, 8.8) and 10.66 (s, 1H, OH).

‡ After alkali washing a trace amount of compound **4a** was obtained from this extract.

§ As an example of a direct hydroxylation into a benzene ring, the formation of 2-nitrophenol by treatment of nitrobenzene with KOH is known.[9]

group on the benzene nucleus, are not clear yet. A tentative mechanism of the acetylenic bond formation is shown in Scheme 3 which illustrates the formation of an anion by Bu^tO^- and succeeding oxidation of the anion by triplet oxygen dissolved in DMF. Attempts to obtain the corresponding diphenylacetylenes from the other stilbenes **3**, R = H, Me, Cl, and Br) have been so far impossible except for the bromo-compound which gave trace amounts of compound (**4**, R = Br), which was assigned from its mass spectral data. It is supposed that the presence of such substituents leads to electronic perturbation on both benzene rings. Further studies concerning the extension and mechanism of the reaction are under way.

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