

DIPHENOXYETHYNE: A HIGHLY ELECTROPHILIC ACETYLENE DIETHER

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Summary: Diphenoxyethyne, the first diaryloxyacetylene so far described in the chemical literature, has been synthesized from 1,2-diphenoxyethane in a five-step sequence; the compound is a highly electrophilic species that adds even poor nucleophiles, such as tert-butoxide and bis-(trimethylsilyl)amide.

None of the methods described for the preparation of dialkoxyethynes¹ provides a practicable entry to the hitherto unknown diaryloxy analogues. However, diphenoxyethyne is of great interest as a substrate to investigate the effects, on the reactivity of the triple bond, of the $p \rightarrow \pi$ delocalization of the oxygen lone-pairs into the aromatic nuclei. In contrast to the dialkoxyethynes, which are very reactive versus electrophiles^{1,2}, one could expect that the triple bond of diphenoxyethyne should become very sensitive to nucleophiles.

In the present communication we wish to report a very simple -but partially succesful, nevertheless- synthesis of diphenoxyethyne (1) that proceeds in five steps from 1,2-diphenoxyethane (Scheme 1).

1,2-Diphenoxyethane (2) was treated, in benzene solution, with an excess of tert-butyl hypochlorite under photochemical conditions (100 W incandescent lamp) to give 1-chloro-1,2-diphenoxyethane (3) (with the characteristic pattern of an ABX system), together with small amounts of 1,2-dichloro-1,2-diphenoxyethane and some unreacted starting material (91% yield of a 10:1:1 mixture). Dehydrochlorination of the crude reaction mixture with KO^tBu in ether solution afforded 1,2-diphenoxyethene (4) (mixture of E and Z isomers), in 89% yield, a compound already synthesized from ethylene chlorohydrin in a seven-step sequence involving high pressure and high temperature conditions³.

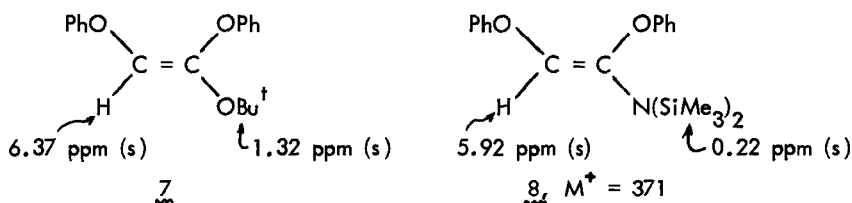
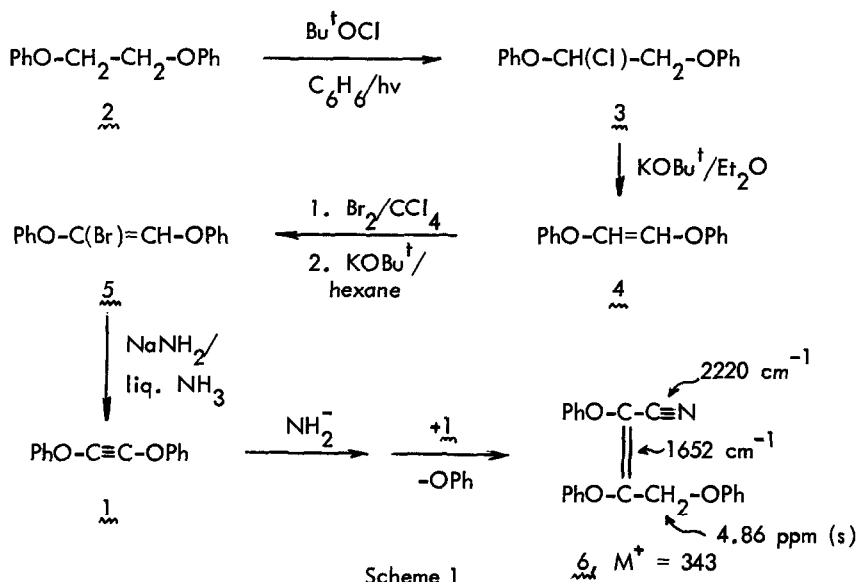
1,2-Diphenoxyethene was treated with bromine in CCl_4 solution and the crude isomeric mixture of rac and meso-1,2-dibromo-1,2-diphenoxyethane was hydrobrominated with KO^tBu in hexane to give (Z)-(E)-1-bromo-1,2-diphenoxyethene (5) in 76% overall yield⁴. Further dehydrobromination with NaNH_2 in liquid NH_3 gave the expected diphenoxyethyne (1). However, owing to the sensitivity of the triple bond to nucleophiles, diphenoxyethyne was isolated only in minute amounts, the dimeric nitrile 6 being the main product instead.⁵

Diphenoxyethyne, that could be isolated by preparative t.l.c. on alumina as a stable, low melting solid, was characterized by mass spectrometry (M^+ 210, 181, 153, 133, 105 and 77).

Attempts to improve the yields by using less nucleophilic bases, such as $\text{KO}^t\text{Bu}/18\text{-crown-6}$ ⁶, or even highly hindered amides, such as $\text{NaN}(\text{SiMe}_3)_2$ ⁷, in THF, led exclusively to the corresponding addi-

tion products 7 and 8. In the former case, only the Z isomer was attacked since cis eliminations are inhibited in the presence of crown ethers ⁸.

On the other hand, neither 1,5-diazabicyclo(4.3.0)non-5-ene (DBN) nor KH in THF are suitable bases to promote the dehydrobromination of 1-bromo-1,2-diphenoxyethene (5).



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