

In situ Generation and Reactions of Hexynylcyanoketene

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Hexynylcyanoketene (**3**) can be formed *in situ* by the pyrolysis of 2,5-diazido-3,6-dihexynyl-1,4-benzoquinone (**2**); the use of (**3**) in the preparation of hexynyl-substituted alkenes and heterocyclic compounds, e.g. β -lactams, is described.

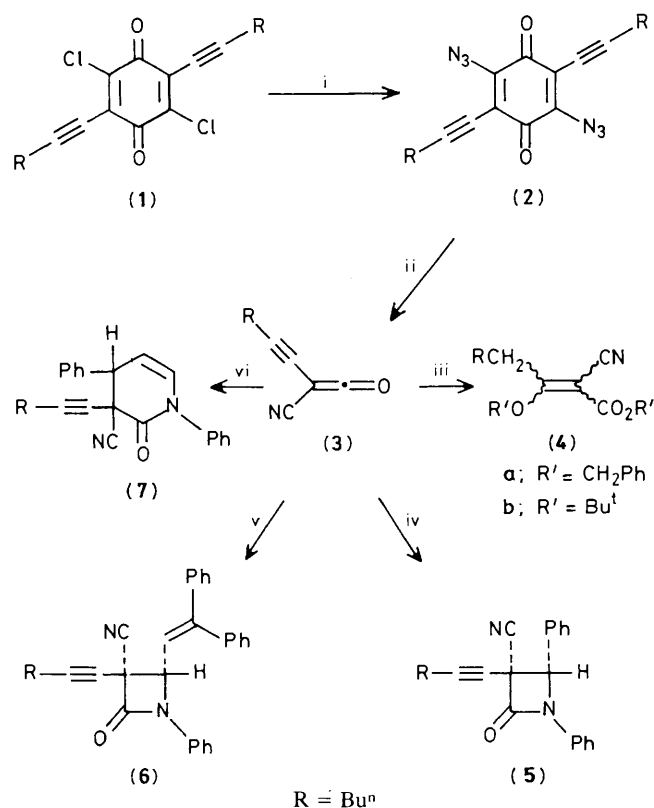
Reported here is the *in situ* generation of hexynylcyanoketene (**3**) which, to our knowledge, represents the first reported example of an alkynylketene.¹ Such cumulenes may be of some synthetic importance since their cycloaddition reactions would provide simple routes to a variety of molecules containing the synthetically versatile alkyne moiety. This would be particularly true for the cyanoketene derivatives since other examples of these electron-deficient ketenes have been observed to be exceptionally reactive and to add to a variety of ketenophiles.²

Although the alkynylketene, (**3**), is the only example reported here, the synthetic route described is expected to be quite general since the alkynylquinone precursors are easily prepared.^{3,4} Specifically, hexynylcyanoketene (**3**) was generated, *in situ*, when 2,5-diazido-3,6-dihexynyl-1,4-benzoquinone (**2**)[†] was pyrolysed at 80 °C in benzene (81% conversion) (Scheme 1).⁵ The diazide, (**2**), was prepared from 2,5-dichloro-3,6-dihexynyl-1,4-benzoquinone (**1**),[†] a member of a series of alkynylquinones for which a general synthetic route has been provided.³

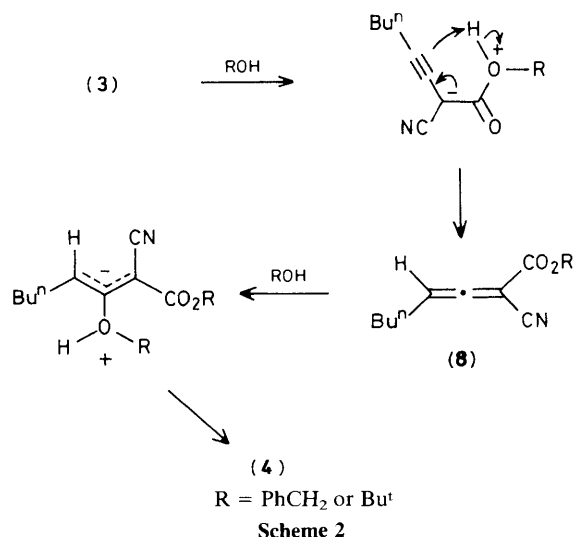
A most unusual transformation was observed when the ketene was generated in the presence of an excess of benzyl alcohol (10 equiv.). This gave a 60% isolated yield of the alkene (**4a**)[†] as a 3:1 mixture of geometric isomers.[‡] The stereoselectivity of the reaction was increased when the alcohol was *t*-butyl alcohol; in this case the alkenes (**4b**)[†] were obtained in 30% isolated yield in an isomeric ratio of 8:1. These transformations most likely involve the formation and subsequent trapping of the allene intermediate, (**8**), as outlined in Scheme 2. Indeed, an absorption band at 1950 cm⁻¹ in the i.r. spectrum of the crude reaction mixture gave evidence for the presence of an allene. This absorption was particularly evident when only one equivalent of *t*-butyl alcohol was employed and disappeared when the crude reaction mixture was treated with an excess of the alcohol. Thus, the intermediacy of (**8**) in this reaction is most likely.

When the ketene was generated in the presence of 1.1 equiv. of *N*-benzylideneaniline or *N*-(δ -phenylcinnamylidene)aniline, the respective β -lactams, (**5**) and (**6**),[†] were obtained in 81% and 52% yields; when the imine was *N*-cinammylideneaniline a 2 + 4 cycloaddition resulted and

the major product, (**7**),[†] was obtained in 62% yield. The stereochemistries of (**5**) and (**6**) were not determined, but are tentatively assigned as (*Z*) on the basis of results obtained



Scheme 1. Reagents: i, N₃⁻, acetone; ii, C₆H₆, 80 °C; iii, PhCH₂OH or Bu^tOH; iv, PhN=CHPh; v, PhN=CHCH=CPh₂; vi, PhN=CHCH=CPh.



[†] Spectral data ¹H n.m.r. δ (CDCl₃): (**1**) (m.p. 129–130 °C) 0.95 (t, *J* 7 Hz, 6H), 1.43–1.71 (m, 8H), 2.59 (t, *J* 7 Hz, 4H); (**2**) (m.p. decomp. >100 °C) 0.94 (t, *J* 7 Hz, 6H), 1.40–1.68 (m, 8H), 2.57 (t, *J* 7 Hz, 4H); (**4a**) (oil) 0.84–0.93 (m, 3H), 1.22–1.69 (m, 6H), 2.92–3.01 (m, 2H), 5.23 (s, 4H), 7.23–7.42 (m, 10H); (**4b**) (oil) 0.87–0.92 (m, 3H), 1.29–1.78 (m, 24H), 2.87–2.93 (m, 2H); (**5**) (m.p. 119–120 °C) 0.92 (t, *J* 7 Hz, 3H), 1.34–1.61 (m, 4H), 2.30 (t, *J* 7 Hz, 2H), 5.24 (s, 1H), 7.10–7.48 (m, 10H); (**6**) (oil) 0.92 (t, *J* 7 Hz, 3H), 1.34–1.53 (m, 4H), 2.25 (t, *J* 7 Hz, 2H), 4.72 (d, *J* 10 Hz, 1H), 6.16 (d, *J* 10 Hz, 1H), 7.08–7.53 (m, 15H); (**7**) (oil) 0.87 (t, *J* 7 Hz, 3H), 1.24–1.52 (m, 4H), 2.03–2.26 (m, 2H), 4.07–4.31 (m, 1H), 5.41–5.55 (m, 1H), 6.47–6.55 (m, 1H), 7.29–7.49 (m, 10H). The analytical and i.r. spectroscopic data for these compounds were in accord with their assigned structures.

[‡] The stereochemistry of the major isomer was not established, but is assumed to be (*Z*) on the basis of mechanistic considerations.

from analogous cycloadditions in which chlorocyanoketene was added to the same imines. It is of interest to note that (5) and (6) appear to represent the first reported examples of 3-alkynylazetidin-2-ones. It is expected that these will function as precursors to a large variety of functionalized 3-cyanoazetidin-2-ones, a class of compounds which have been observed to show marked antibacterial as well as antifungal properties.⁶

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