Sesquiacetylenic and Allenic Structures of Prop-2-ynyl Dianions

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Summary Addition of hexamethylphosphoric triamide to solutions of prop-2-ynyl dilithio-derivatives causes the disappearance of their strong i.r. absorption bands at 1800—1900 cm^{-1} and the appearance of a medium new band at *ca.* 2050 cm^{-1}, indicating that a structure transformation from an allenic to a sesquiacetylenic form has taken place.

THE dimetallation of internal acetylenes by abstraction of both protons from the same prop-2-ynyl position[1] led to an assignment of a "sesquiacetylenic" structure (I) for the dianions.[2] In this structure a maximum overlap between all orbitals is present, see (A), when the three atoms of the system and the two linked to them have a linear arrangement. A different structure, the allenic form (II), was assigned by West and Jones[3] to polylithiated acetylenes. SCF–MO calculations of the CNDO/2 type marginally favour[4] (I) over (II) and the sesquiacetylene dilithio-derivative (III) over the allenic form (IV).

We report the i.r. data (Table) of dilithiated internal acetylenes in several solvents which support the view[5] that these compounds can exist either in the sesquiacetylenic or the allenic form, according to conditions.

Table

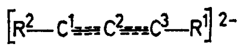
Compound	Absorption bands (cm^{-1})	Solvent
$[\mathrm{PhC}\vdots\mathrm{C{\cdot}CH}]\mathrm{Li}_2$	1895s	Hexane or ether
,,	2080w, 1895	THF
,,	2045m	HMPT[a]
$[\mathrm{PhC}\vdots\mathrm{C{\cdot}C}]\mathrm{Li}_3$	1800	Hexane or ether
,,	2045	HMPT
$[\mathrm{PhC}\vdots\mathrm{C{\cdot}CMe}]\mathrm{Li}_2$	1795s	Hexane or ether
,,	1795, 2000—2040m	Hexane + TMEDA[a]
,,	2075	THF
$[\mathrm{PhC}\vdots\mathrm{C{\cdot}CHMe}]\mathrm{Li}$	1870	Hexane or ether
$[\mathrm{PhC}\vdots\mathrm{C{\cdot}CHPh}]\mathrm{Li}$	1870	Hexane or ether
$[\mathrm{PhC}\vdots\mathrm{C{\cdot}CPh}]\mathrm{Li}_2$	1790	Hexane
,,	1790, 2050	Ether
,,	1790, 2075m	Hexane + TMEDA
,,	2075m	TMEDA

[a] HMPT = hexamethylphosphoric triamide; TMEDA = tetramethylethylenediamine.

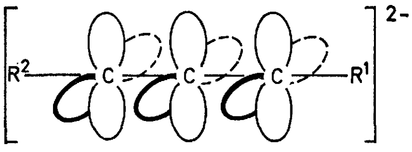
The presence of the dilithio-derivative in all the solutions was proved by treatment with trimethylchlorosilane and identification of the bis-trimethylchlorosilyl derivatives of the compounds studied.[2]

A change to more co-ordinating solvents produces a shift in the position of the absorption band from *ca.* 1800 to 2050 cm^{-1}. This change takes place more readily with the more symmetrical acetylenes. The most drastic change is produced by HMPT and TMEDA.

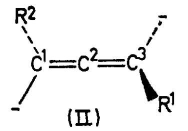
The changes in the position of the absorption bands with the change in solvent can be ascribed to a change from the allenic structure (IV) (which is presumably present in less co-ordinating solvents) to the sesquiacetylenic form, probably (III) (which would be favoured in the strongly co-ordinating ones). In relatively non-polar solvents, the lithium atoms form bonds that are largely covalent, thus stabilizing (IV). When co-ordination of the lithium atoms with the solvent gets stronger, the covalency with carbon is less (the coulombic interactions in the ion pair is also weakened) and the negative charges are more concentrated on the three-carbon segment. These charges are stabilized by delocalisation in the sesquiacetylenic structure. This delocalization makes the carbon–carbon bonds stronger and is probably the cause of the shift of the absorption bands to higher frequencies.



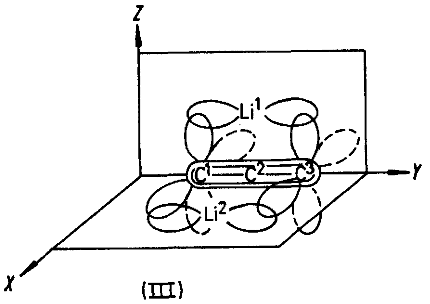
(I)



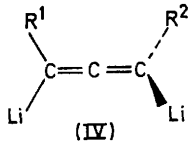
(A)



(II)



(III)



(IV)

The exact structure of the dilithio-derivatives in strongly co-ordinating solvents is not known. It could be (III) with the lithium atoms externally solvated or the cations may be solvent separated from the anions.[6]

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[2] J. Klein and S. Brenner, *J. Amer. Chem. Soc.*, 1969, **91**, 3094; *Tetrahedron*, 1970, **26**, 2345.

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[4] J. Y. Becker, A. Y. Meyer, and J. Klein, *Theor. Chim. Acta*, 1973, **29**, 313.

[5] J. Klein and S. Brenner, *Tetrahedron*, 1970, **26**, 5807.

[6] J. Smid, *Angew. Chem. Internat. Edn.*, 1972, **11**, 112.