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THE STEREOCHEMISTRY OF THE INTERMEDIATE VINYLIC RADICAL IN THE RADICAL CYCLIZATION OF 6-HALO-1-PHENYL-1-HEXYNES. EVIDENCE FOR LINEAR 1-PHENYLVINYLIC RADICALS

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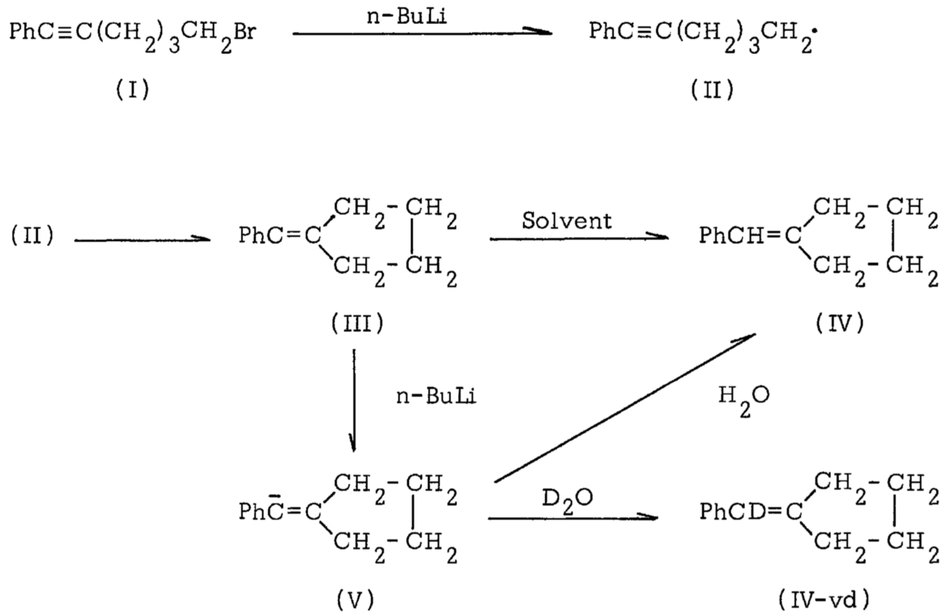
Reaction of 6-bromo-1-phenyl-1-hexyne-6,6-d_2 with n-butyllithium gave (E)- and (Z)-2-benzylidenecyclopentane-1,1-d_2 in equal amounts by way of radical cyclization, and 6-iodo-1-phenyl-1-hexyne-3,3-d_2 with tri-n-butyltin hydride afforded similarly the same product mixture. These results are explained in terms of a linear 1-phenylvinylic radical with an sp-hybridized radical centre and a half-filled p orbital conjugated with the phenyl group.

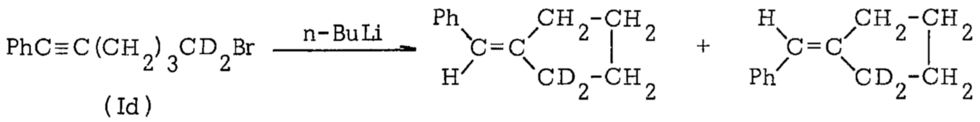
We have shown that the radical cyclization of 1-ethoxy-6-iodo-1-hexyne to give ethoxymethylenecyclopentane involves intermediate 1-ethoxyvinylic radicals in a bent form, in which the half-filled sp^2-hybrid orbital is situated trans to the added carbon group.[1)] However, the possibility of a linear vinylic radical, in which the radical centre is sp-hybridized and the odd electron occupies a p-orbital, is of interest especially with a species carrying a conjugating group such as a phenyl at the radical centre, since the odd electron can be delocalized into the benzene nucleus, if the latter lies perpendicular to the plane of the double bond, thus leading to the stabilization of the radical.[2)] Although the 1,2-diphenylvinyl radical was trapped in a bent form in the thermal decomposition of t-butyl cis- and trans-α-phenylperoxycinnamate,[3)] the possibility of a linear form has not been completely ruled out. In fact, Kopchik and Kampmeier have suggested that the 1,2-diphenylvinyl radical is linear on the ground of analysis of experimental data together with molecular-orbital calculations (extended Hückel method) using the 1-vinylvinyl radical as a model.[4) The present communication presents evidence for the existence of 1-phenylvinylic radicals in a linear form.

The reaction of 6-bromo-1-phenyl-1-hexyne (I, 3.5 mmoles) with n-butyllithium (4.0 mmoles) in 6 ml of a n-hexane-ether mixture (5 : 1) at temperature below 40° followed by hydrolysis with deuterium oxide gave benzylidenecyclopentane (IV, 24%), which contained 23% of deuterium, together with 1-phenyl-1-decyne (17%) and 1-phenyl-1-hexyne (2%). Such a reaction had originally been carried out by Ward, who had produced evidence for involvement of radicals as intermediates, thus, 6-phenyl-5-hexynyl radicals (II) cyclizing to give cyclopentylidenebenzyl radicals (III).[5) Thus, the reaction steps are shown in the accompanying chart, in which the deuteriated benzylidenecyclopentane (IV-vd) is formulated as produced via an organolithium intermediate (V), a carbanion species, produced by electron transfer to the intermediate radical (III).



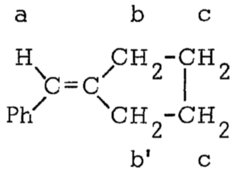
For the present stereochemical study, the reaction was similarly carried out with 6-bromo-1-phenyl-1-hexyne-6,6-d_2 (Id) and the cis to trans ratio of isotopically isomeric benzylidenecyclopentanes (IVd) finally produced was examined. The deuterio-compound, 6-bromo-1-phenyl-1-hexyne-6,6-d_2 (Id), $C_{12}H_{11}D_2Br$, bp 96-97° (0.15 mm), was obtained by reduction of

6-phenyl-5-hexynoic acid, bp 118-120° (0.1 mm), with lithium aluminium deuteride followed by treatment of the resulting 1-phenyl-1-hexyn-6-ol-6,6-d_2, bp 103-105° (0.15 mm), with phosphorus tribromide. The quantitative incorporation of deuterium at position 6 in Id was established from its nmr spectrum by the absence of a signal (δ 3.35) due to the bromomethyl protons of 6-bromo-1-phenyl-1-hexyne (I). A reaction mixture of the deuteriated bromohexyne (Id) with an excess of n-butyllithium (1.5 moles per mole of Id) was treated with carbon dioxide in order to remove metalated benzylidenecyclopentane (Vd) by converting it into the corresponding carboxylate and then with water, and 2-benzylidenecyclopentane-1,1-d_2(IVd), which was formed exclusively by the homolytic pathway, was isolated. The ratio in which syn and anti adducts (E-IVd and Z-IVd)$^{6)}$ were formed was determined by nmr measurements as follows.



(Id) (E-IVd) (Z-IVd)

In the nmr spectrum of benzylidenecyclopentane (IV) in carbon tetrachloride the signals from methylene groups b and b' appear at about δ 2.24 as broad overlapping multiplets. When other protons, a and c, are irradiated for decoupling, the signals from b and b' are resolved into two

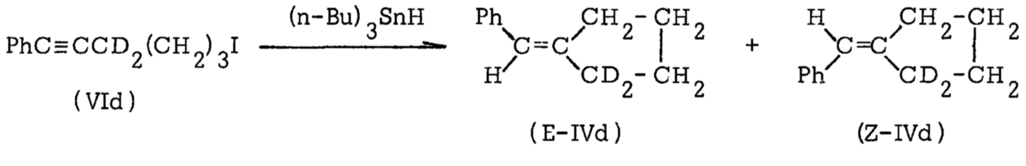


(IV)

peaks 5 Hz apart (with a 100 MHz apparatus). The assignment of the peaks has been made by analogy with the spectra of cis- and trans-β-methylstyrene,$^{7)}$ the difference in shift of methyl resonance being attributable to the ring current effect. The nmr spectrum of 2-benzylidenecyclopentane-1,1-d_2 (IVd) obtained above, when measured under irradiation in the same way, showed two peaks identical with those due to methylenes b and b' in IV in respect of the shift, shape and relative height.

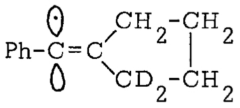
The nmr spectrum of IVd obtained by the reaction of Id with an excess of n-butyllithium (3.3 moles per mole of Id) followed by hydrolysis with water also showed the same signals in appearance when measured under irradiation, although a separate experiment with deuterium oxide showed that 33% of IVd was derived from anionic species V. These findings indicate that the cyclic adduct (IVd), whether it is derived from the radical intermediate (III) or from the carbanionic one (V), contains the syn and anti isomers (E-IVd and Z-IVd) in equal amounts.

The same stereochemical result was obtained in the cyclization of radicals generated from 6-iodo-1-phenyl-1-hexyne-3,3-d_2 and tri-n-butyltin hydride. Cyclization of 6-phenyl-5-hexynyl radicals (II) had been observed in the reduction of 6-bromo-1-phenyl-1-hexyne (I) with tri-n-butyltin hydride.[8)] In fact, reaction of 6-iodo-1-phenyl-1-hexyne (VI, 5.6 mmoles) with tri-n-butyltin hydride (6.0 mmoles) in 100 ml of tetrahydrofuran at 60° for 20 hrs in the presence of azobisisobutyronitrile (0.1 mmole) gave benzylidenecyclopentane (IV, 88%) and 1-phenyl-1-hexyne (5%). We carried out this reaction starting with 6-iodo-1-phenyl-1-hexyne-3,3-d_2 (VId), $C_{12}H_{11}D_2I$, bp 105-107° (0.15 mm), which was obtained by condensing 1-bromo-4-chlorobutane-1,1-d_2 with sodium phenylacetylide followed by treatment of the resulting 6-chloro-1-phenyl-1-hexyne-3,3-d_2, $C_{12}H_{11}D_2Cl$, bp 83-85° (0.4 mm), with sodium iodide in acetone. Treatment of the deuterio-iodide (VId) with tri-n-butyltin hydride gave 2-benzylidenecyclopentane-1,1-d_2 (IVd) as a colourless oil. Its nmr spectrum when measured under irradiation for decoupling as mentioned above showed two peaks of signals, the same in appearance as those obtained with benzylidene-cyclopentane, indicating that the syn and anti adducts (Z-IVd and E-IVd) were formed in equal amounts.

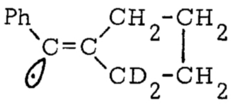


The possibility that this result might have been brought about by the isomerization of the syn or anti adduct (Z-IVd or E-IVd) initially formed caused by reversible addition of organotin radicals to olefins[9)] is ruled out by separate experiments, in which the reaction of 6-iodo-1-phenyl-1-hexyne (VI) with tri-n-butyltin hydride was carried out in the presence of cis- and trans-β-methylstyrene and these olefins were then recovered in 80% yield with almost complete retention of the original configurations.

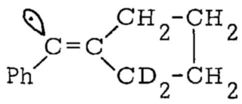
We have shown that the cyclization of 6-ethoxy-5-hexynyl radical takes place stereoselectively in the anti fashion to yield a vinylic radical, in which the half-filled sp^2 hybrid orbital is disposed trans to the added carbon group.1) In view of this observation, it is irrational to suppose that the 6-phenyl-5-hexynyl-1,1-d_2 radical (IId) cyclizes in the syn (E-IIId) as well as in the anti fashion (Z-IIId), both to the same extent, to give finally the cis and trans adducts (E-IVd and Z-IVd) in



(lin-IIId)



(E-IIId)



(Z-IIId)

equal amounts. Another possibility that the 6-phenyl-5-hexynyl-1,1-d_2 radical cyclizes exclusively in the anti fashion to give the vinylic radical in a bent form (Z-IIId) and this form isomerizes very quickly to another bent form (E-IIId), the two forms in rapid interconversion thus giving rise to an equimolecular mixture of the final addition products (E-IVd and Z-IVd), is highly unlikely, because the 1,2-diphenylvinyl radical has been shown to be rather slow in isomerization compared with abstraction.3) It is therefore concluded that the cyclization of 6-phenyl-5-hexynyl-1,1-d_2 radicals (IId) yields the vinylic radical in a linear form (lin-IIId). The argument is the same with the 6-phenyl-5-hexynyl-4,4-d_2 radical. It cannot be decided, however, whether the linear radical (lin-IIId), as such, abstracts a hydrogen atom with equal probability on both sides of the p-orbital lobe or the energy barrier between the linear form (lin-IIId) and the bent form (E-IIId and Z-IIId) is so low that the linear form, when generated, rapidly collapses to equal amounts of cis- and trans-bent form (E-IIId and Z-IIId) before hydrogen abstraction.

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