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ELECTROREDUCTIVE CYCLIZATION OF ACETYLENIC HALIDES AT MERCURY CATHODES

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Chemical reductants such as tri-n-butyltin hydride in benzene, lithium biphenyl in tetrahydrofuran, and n-butyllithium in a hexane-ether solvent mixture can promote the intramolecular cyclization of certain acetylenic halides.[1-4] For example, reduction of 6-bromo-1-phenyl-1-hexyne with any of the previously named reagents results in the formation of benzylidenecyclopentane.[1-3] Similarly, hydrolysis of a tetrahydrofuran solution of the Grignard reagent prepared from 7-chloro-2-heptyne produces a 90% yield of ethylidenecyclopentane.[4]

To determine if the cyclization of acetylenic halides can be induced electrochemically, and to ascertain the effects caused by selective reduction of either the carbon-carbon triple bond or the carbon-halogen site, we have examined the behavior of 6-bromo-1-phenyl-1-hexyne, 1-bromo-5-decyne, and 6-chloro-1-phenyl-1-hexyne at mercury cathodes in anhydrous N,N-dimethylformamide containing 0.05 F tetra-n-butylammonium perchlorate as supporting electrolyte. Interestingly, although carbocyclic products formed from chemical reduction of these three acetylenic halides are always ylidenecyclopentanes,[1-4] electrochemical reduction may lead to five-membered carbocycles only, to six-membered carbocycles only, or to both five- and six-membered carbocycles.

A polarogram for reduction of 6-bromo-1-phenyl-1-hexyne exhibits three waves with half-wave potentials of -2.35, -2.60, and -2.80 V vs. SCE (aqueous saturated calomel reference electrode). Under comparable conditions, the polarographic reduction of n-hexyl bromide occurs in a single step with a half-wave potential of -2.29 V,[5] and the reduction of 1-phenyl-1-hexyne was found in the present research to be a two-step process with half-wave potentials of -2.65 and -2.88 V. Accordingly, we associate the first polarographic wave for 6-bromo-1-phenyl-1-hexyne with reduction of the carbon-bromine bond, whereas the second and third waves result from the stepwise reduction of the phenyl-activated carbon-carbon triple bond.

At potentials between -2.3 and -2.5 V, the carbon-bromine bond of 6-bromo-1-phenyl-1-hexyne can be reduced without direct attack on the carbon-carbon triple bond. Several electrolyses were performed at controlled potential under a nitrogen atmosphere in a conventional three-electrode cell, the potential of the mercury pool cathode being kept at -2.45 V; one electron per molecule of starting material was involved in the reduction process. Extraction of the electrolysis products into ether, followed by gas chromatographic separation and identification of the various compounds, revealed the presence, on the average, of 58% 1-phenyl-1-hexyne, 14% 1-phenylcyclohexene, 12% benzylidenecyclopentane, and 9% 1-phenyl-1-hexyne-5-ene, all yields being relative to the original quantity of acetylenic halide. Small amounts, never exceeding 5%, of 1-phenyl-1-hexene, cyclohexylbenzene, and benzylcyclopentane were obtained as well.

Electrolysis of a solution of 6-bromo-1-phenyl-1-hexyne at -2.60 V causes reduction of both the carbon-bromine bond and the carbon-carbon triple bond, and formation of an intense green coloration, probably due to a relatively stable phenyl-conjugated radical. A preliminary study in which the acetylenic halide was reduced electrochemically in the cavity of an esr spectrometer suggests that the colored specie may be the radical precursor of benzylidenecyclopentane. Three electrons per molecule of the acetylenic halide were involved in the reaction, and gas chromatographic analysis indicated higher yields of carbocyclic products than formed by reduction of just the carbon-bromine bond — cyclohexylbenzene (23%), benzylidenecyclopentane (20%), 1-phenylcyclohexene (11%), 1-benzylcyclopentene (7%), 1-phenyl-1-hexyne (17%), and 1-phenyl-1-hexene (13%), plus small percentages of benzylcyclopentane and 1-phenylhexane. When 6-bromo-1-phenyl-1-hexyne is exhaustively reduced at -2.85 V, 1-phenylhexane is the sole product.

An isolated acetylenic bond is electrochemically inert, so 1-bromo-5-decyne exhibits only one polarographic wave, with a half-wave potential of -2.45 V, for reduction of the carbon-bromine bond. Three large-scale reductions of 1-bromo-5-decyne at -2.70 V, each involving one electron per molecule, yielded 5-decyne (59%) and 1-n-butylcyclohexene (38%). Due to the electroinactivity of alkyl chlorides, 6-chloro-1-phenyl-1-hexyne shows no polarographic wave for reduction of the carbon-chlorine bond. However, the carbon-carbon triple bond is reducible in an ill-defined stepwise fashion; the pair of two-electron reductions appears almost as a single wave with a half-wave potential of -2.70 V. Reduction of 6-chloro-1-phenyl-1-hexyne at -2.60 V involved 3.7 electrons per molecule, and as products 45% benzylcyclopentane, 23% 1-phenylhexane, 15% 1-phenyl-1-hexyne, 13% 1-phenyl-1-hexene, and 4% benzylidenecyclopentane were obtained.

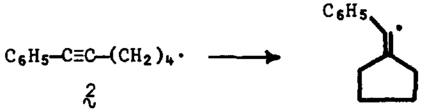
To account for five-membered carbocycles and straight-chain compounds among the electrolysis products, we propose that homogeneous reactions occur after cathodic reduction which are identical to those seen with chemical reductants.[1-4] Reduction of 6-bromo-1-phenyl-1-hexyne at

-2.45 V appears to be a one-electron process which yields an alkyl radical and bromide ion

$$C_6H_5{-}C{\equiv}C{-}(CH_2)_4Br \;+\; e \longrightarrow C_6H_5{-}C{\equiv}C{-}(CH_2)_4\cdot \;+\; Br^-$$

1 2

after which the alkyl radical can form 1-phenyl-1-hexyne by hydrogen atom abstraction, can disproportionate to produce 1-phenyl-1-hexyne-5-ene and 1-phenyl-1-hexyne, or can react intramolecularly to give the precursor of benzylidenecyclopentane:



2 3

A similar set of reactions has been postulated for reduction of 6-bromo-1-phenyl-1-hexyne with lithium biphenyl in tetrahydrofuran.[2,3] Most likely, 1-phenyl-1-hexene and benzylcyclopentane result from electroreduction of 1-phenyl-1-hexyne and benzylidenecyclopentane, respectively.

During electrolysis of 6-bromo-1-phenyl-1-hexyne at -2.60 V, both the carbon-bromine bond and the carbon-carbon triple bond are reducible. Thus, in addition to the above reactions, there can be formation of a phenylacetylene radical anion (or the corresponding dianion)

$$C_6H_5{-}C{\equiv}C{-}(CH_2)_4Br \;+\; e \longrightarrow C_6H_5{-}\dot{C}{=}\bar{C}{-}(CH_2)_4Br$$

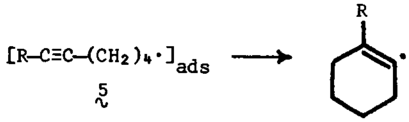
1 4

which may yield radical 3 (or its anionic counterpart) by an intramolecular carbanion displacement on the bromine center;[2] this process appears to be more efficient than cyclization of radical 2, since larger amounts of five-membered carbocycles result from reduction of the carbon-carbon triple bond. Rearrangement of radical 3, prior to hydrogen abstraction, could lead to 1-benzylcyclopentene, which was found among the products of electrolysis at -2.60 V.

Our findings for 1-bromo-5-decyne and 6-chloro-1-phenyl-1-hexyne substantiate these conclusions. With the former compound, five-membered carbocycles are not favored because cyclization of $C_4H_9{-}C{\equiv}C{-}(CH_2)_4\cdot$ cannot lead to a resonance-stabilized specie such as radical 3; furthermore, since $C_4H_9{-}\dot{C}{=}\bar{C}{-}(CH_2)_4Br$ is not produced, there can be no intramolecular carbanionic displacement of bromide to yield n-pentylidenecyclopentane. With 6-chloro-1-phenyl-1-hexyne, five-membered carbocycles arise because $C_6H_5{-}\dot{C}{=}\bar{C}{-}(CH_2)_4Cl$ can cyclize by intramolecular displacement of chloride; moreover, the absence of chlorine-containing products implies that $C_6H_5{-}\dot{C}{=}\bar{C}{-}(CH_2)_4Cl$ undergoes an intermolecular radical-transfer process, by reaction with $C_6H_5{-}C{\equiv}C{-}(CH_2)_4Cl$, to form Cl^- and $C_6H_5{-}C{\equiv}C{-}(CH_2)_4\cdot$, which abstracts hydrogen and is further reduced at a mercury cathode.

In fact, the same intermolecular radical-transfer reaction could occur with 6-bromo-1-phenyl-1-hexyne, but its effect would be masked because the carbon-bromine bond is electroactive.

Six-membered carbocycles are unique to the electrochemical reduction of 6-bromo-1-phenyl-1-hexyne and 1-bromo-5-decyne, and have not been detected as products of chemically induced cyclization.[1-3] We believe that the presence of an electrode phase is essential to the formation of substituted cyclohexenes, and that either of two mechanisms can account for these species. First, the alkyl radical produced by reduction of the carbon-bromine bond may be adsorbed upon the surface of the mercury cathode,[6] in which state cyclization might differ stereochemically from the homogeneous reactions observed with chemical reductants:[4]



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Following hydrogen abstraction, 1-phenylcyclohexene could be reduced to cyclohexylbenzene; but the isolated carbon-carbon double bond of 1-*n*-butylcyclohexene is not reducible. Second, six-membered carbocycles might be formed from organomercury intermediates such as $R{-}C{\equiv}C{-}(CH_2)_4Hg\cdot$, $R{-}C{\equiv}C{-}(CH_2)_4HgBr$, or $[R{-}C{\equiv}C{-}(CH_2)_4]_2Hg$.[6] Apparently, six-membered carbocycles do not originate from five-membered carbocycles because, as the products of the electrochemical reduction of α-iodobenzylidenecyclopentane, we found only benzylidenecyclopentane and 1-benzylcyclopentene. Reduction of 6-chloro-1-phenyl-1-hexyne yields no six-membered carbocycles, which we attribute to the fact that, because the carbon-chlorine bond is not reduced directly, no adsorbed alkyl radicals or organomercury species are produced.

Further work is planned to elucidate the electrochemical cyclization processes in greater detail.

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