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THE SYNTHESIS OF SPIRO[2,3]HEXENES
AND A SPIRO[2,3]HEXADIENE

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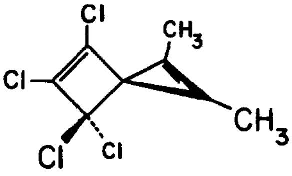
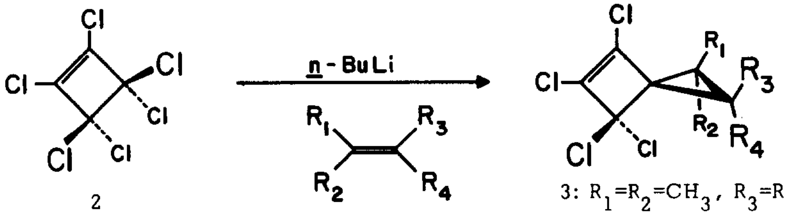
Carbon rings in a spiro arrangement have been the subject of many synthetic(1) and theoretical exercises.(2) Special interest has centered on spiropolyenes where the possibility exists of π-orbital overlap between π-bonds in spiro-connected rings, for which the term spiroconjugation has been used.(2) We wish to report the first example, 1, of a spiro[2,3]-hexa-1,4-diene as well as several examples (structures 3-5) of substituted spiro[2,3]hex-4-enes. The molecules are easily prepared, relatively stable, and possess functionality which should allow the testing of proposals for spiroconjugation.



1

Reaction of hexafluorocyclobutene(3) with aluminum chloride in dichloromethane gave as the sole product in 90% yield, hexachlorocyclobutene, 2, the key intermediate in the synthesis of the spiro compounds. On treatment with an alkyllithium reagent in hexane or hexane-ether at low temperature in the presence of an alkene or an alkyne, formal carbene occurs (eq 1).

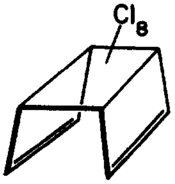


2

eq 1

3: $R_1=R_2=CH_3$, $R_3=R_4=$ H
4a: $R_1=R_3=CH_3$, $R_2=R_4=$ H
4b: $R_1=R_3=$ H , $R_2=R_4=CH_3$
5: $R_1=R_4=$ H , $R_2=R_3=CH_3$
(and its enantiomer)

A typical procedure follows: To a solution of hexachlorocyclobutene (20.00 g, 76.5 mmoles) and 2-butyne (50 ml, ca. 700 mmoles, Farchan Chemical Co.) in 500 ml of dry pentane under nitrogen at -30° (nitromethane slush bath) was added a solution of n-butyllithium in hexane (1.6 M, 70 ml, 112 mmoles of n-butyllithium). Addition was dropwise over one hr. The resulting suspension of colorless solid in a yellow solution was stirred at -30° for one hr and allowed to warm to 25° over an additional hr. Water (100 ml) was added, the pentane layer was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford a yellow oil, 19.32 g. Short path distillation (50°/0.005 torr) gave a colorless distillate, partially solid at 25°, 11.29 g. Column chromatography of the distillate afforded 1 of >95% purity in 40% overall yield, mp 36-37°.(4) The nonvolatile products from the reaction have not been investigated except for isolation of the dimer 6 of tetrachlorocyclobutadiene, mp 161° [lit(5) mp 160-162° (dec)], in less than 5% yield.



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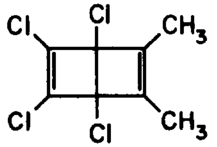

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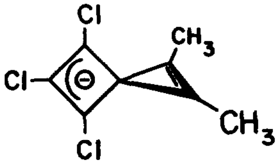
The identification of spirodiene 1 rests primarily on spectral evidence such as a moderate intensity absorption at 1885 cm^{-1} in the infrared spectrum, a position typical of 1,2-dimethylcyclopropenes,(6) and at 1630 cm^{-1} due to the 1,2-dichlorocyclobutene double bond.(7) Nmr (CCl_4): singlet at 2.17δ. Mass spectrum: parent ion at m/e 242 with an isotope pattern consistent with the presence of four chlorine atoms.(8) No change in spirodiene 1 occurs during storage at 0° for many weeks, but slow decomposition is observed at 120° in chlorobenzene solution to give high molecular weight products; it does not isomerize to tetrachloro-o-xylene. An alternative reasonable structure for 1 is 7 which fits qualitatively all the spectral data for 1. However, 7 has been synthesized recently by a different route and clearly is different from 1 (nmr spectra, mp).(7)

The spiro[2,3]hexenes 4a(4) and 4b(4) with cis-1,2-dimethylcyclopropane structures are formed in equal amounts from cis-2-butene and isolated by preparative vpc; none of the trans isomer 5 is observed. Nmr of 4a (CCl_4): 1.28δ (two overlapping doublets, 6H, $-CH_3$); 1.75δ (multiplet, 2H, -CH-). The pattern of the nmr spectrum of 4a is identical with that of 3,3-dichloro-cis-1,2-dimethylcyclopropane.(9) Nmr of 4b (CCl_4): 1.48δ (singlet, accidental degeneracy of all protons). The mass spectra of 4a and 4b are superimposable. The tentative relative structural assignments of 4a and 4b are based on hydrogenation of spiro[2,3]hexadiene 1 (Pd/C, ethyl alcohol, one mole-equivalent of hydrogen uptake at 1 atm) to give one product, identical (nmr, vpc) with 4a; inspection of molecular models of 1 suggests the most accessible direction of hydrogenation would lead to 4a. Isobutylene and trans-2-butene each give only one adduct, the spiro[2,3]hexenes 3(4) and 5,(4) respectively.

Experiments in progress concerning the interaction of the π-orbitals in 1, and the ease of formation and stability of potentially spiroconjugated anion 8 will be reported in due course.



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c. Spiro[2,4]heptatrienes: G. Farges and A. S. Drieding, Helv. Chim. Acta, 49, 552 (1966) and E. T. McBee, G. W. Calundann and T. Hodgins, J. Org. Chem., 31, 4260 (1966). No examples of spiro[2,2]pentadienes have been reported and this note presents the first report of spiro[2,3]hexadienes and spiro[2,3]hexenes that the authors are aware of.

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