

## 09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

I and II respectively.

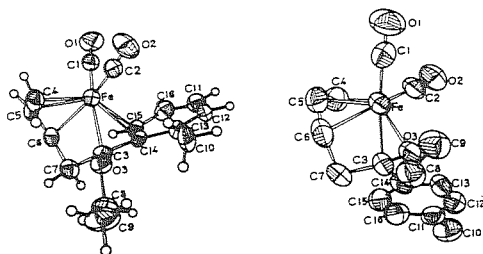
The results of structure analyses show that: In reaction one  $\pi$  bond of each butadiene molecule has been opened with the aid of iron medium so as to cause carbon atom C7 to form a new bond with the "carbene" atom C3 and leave the other three carbon atoms C4, C5 and C6 of butadiene bonded to Fe atom by p- $\pi$  molecular orbital. Both molecular structures satisfy 18-electron rule evidently, but in somewhat different and interesting ways. Very fascinatingly, on the basis of the bond distances and group orientations, it may be established that in molecule I the bonded  $\pi$ -molecular orbital composed by C14 and C15 in benzenering which exhibits certain character of Kekule structure, should overlap with the orbital of Fe, whereas in molecule II, the atom O3 of ethoxy coordinates to iron instead, completing the full valence shell of metal atom.

to indicate Li-Li bonding. The lithium atoms are also symmetrically above and below the plane ( $\pm 0.80$  Å) of the enamine functional groups. This molecular structure corresponds closely to the minimum energy configuration calculated by *ab initio* methods for the lithium enolate of acetaldehyde, thus providing the first experimental proof of this prediction.<sup>1</sup> This structure is totally dissimilar to the x-ray structures of THF-solvated lithium enolates.<sup>2</sup>

The molecular structure of (I) will be presented along with other organolithium derivatives that have been widely used as reactive intermediates in synthetic organic chemistry.

<sup>1</sup>T.J.Lynch, M.Newcomb, D.E.Bergbreiter and M.B.Hall, *J.Org.Chem.*, 1980, 45, 5005.

<sup>2</sup>R.Amstutz, W.B.Schweizer, D.Seebach and J.D.Dunitz, *Helv.Chem.Acta*, 1981, 64, 2617.



(I)

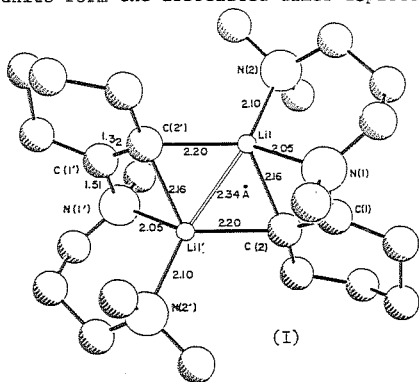
(II)

09.3-3 ORGANOLITHIUM DERIVATIVES - REACTIVE INTERMEDIATES IN ORGANIC SYNTHESIS: A CRYSTALLOGRAPHIC INVESTIGATION.

By Paul G. Williard, Dept. of Chemistry, Brown Univ., Providence, Rhode Island 02912, U.S.A.

N-(2-Lithiocyclohexenyl)-N,N',N'-trimethyl-1,3-propanediamine (I) is a stable solid. This compound is important as the functional equivalent of the enolate anion of cyclohexanone. The crystallographic asymmetric unit of (I) is a monomer of molecular formula  $C_{12}H_{22}LiN_2$ .

The asymmetric units of (I) are sufficiently close to crystallographic inversion centers so that two asymmetric units form the associated dimer depicted.



(I)

The doubly bridging  $sp^2$ -carbons, C(2) and C(2'), are unexceptional and have an analogy in the structures of several aryl lithium derivatives. However, the lithium atoms lie close enough together (2.34 Å)

09.3-4 SOLID STATE POLYMERIZATION OF DIACETYLENES. By V.E.Shklover, Yu.T.Struchkov (Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Moscow, USSR), I.A.Bagirov, I.I.Konstantionov, Yu.B.Amerik (Topchiev Institute of Petrochemistry of the USSR Academy of Sciences, Moscow, USSR)

At present there are crystal structural data on 24 diacetylenes, of which 17 are polymerizable in solid state, and on about 6 polydiacetylenes, formed via the solid state polymerization of corresponding diacetylenes, proceeding (except for one case) by the shearing mechanism, defined by the packing geometry parameters  $S_I$  and  $\gamma_I$  (G.Wegner, *Chemistry and Physics of One-Dimensional Metals*, Plenum, New York, 1977, p.297; R.H.Baughman, *J.Pol.Sci.-Phys.* (1974) 12, 1511).

We carried out a physico-chemical study of a new type of diacetylenes

