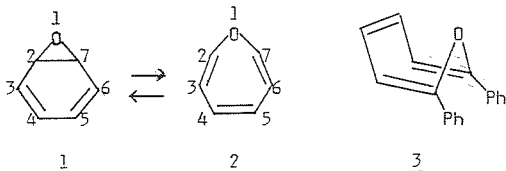


09.2-62 ARENE OXIDE-OXEPIN ISOMERIZATION.

By Deirdre A. Kennedy and John F. Malone, Department of Chemistry, The Queen's University of Belfast, Northern Ireland.

Arene oxide-oxepin ($1\rightleftharpoons 2$) isomerization is probably implicated in the observed racemization of some optically active arene oxides which have biological importance as metabolites of polycyclic aromatic hydrocarbons (PAHs).



As part of a wider structural study of PAH metabolites we have determined the structure of the 2,7-diphenyl derivative of ($1\rightleftharpoons 2$). Crystals are monoclinic, space group $P2_1/n$, with $a = 11.656(12)$, $b = 13.694(14)$, $c = 17.025(17)$, $\beta = 100.82(10)^\circ$, $Z = 8$, $D_x = 1.226$. Although, in the crystal, the asymmetric unit contains two independent molecules, they adopt identical boat conformations of oxepin $\underline{3}$ and differ only marginally in the conformations of the phenyl substituents. Average bond lengths in the oxepin ring are: $O1-C2 = 1.416(3)$, $C2-C3 = 1.347(3)$, $C3-C4 = 1.442(4)$, $C4-C5 = 1.353(6)$. (1880 diffractometer data, $I > 3\sigma(I)$, $R = 0.056$).

This structure and that of the *t*-butyl ester of 2-carboxybenzene oxide-oxepin (monoclinic, $Z = 4$) are discussed in relation to structures predicted by theoretical methods for unsubstituted, monosubstituted and disubstituted benzene oxide-oxepins.

09.2-63 CRYSTAL AND MOLECULAR STRUCTURES OF TWO OXAZAPHOSPHORIN DERIVATIVES. By K.R. Acharya, S.S. Tavale and T.N. Guru Row, Physical Chemistry Division, National Chemical Laboratory, Pune 411008, India.

The derivatives of 1,3,2-Oxazaphosphorinane are clinically useful anti-cancer drugs. The oxazaphosphorinane ring undergoes conformational changes due to steric and electronic influences of the substituents, particularly on the phosphorus and nitrogen atoms. The two structures, 2-chloro-6-(*p*-chlorophenyl)-3-(*p*-tolyl)-3,4-dihydro-1,3,2-oxazaphosphorin-2-oxide(I) and 2-chloro-6-phenyl-3-(*p*-tolyl)-5-methyl-tetrahydro-1,3,2-oxazaphosphorin-2-oxide(II) bring out the effect of the change of conformation in the ring itself, from a cyclohexene type conformation in (I) to a cyclohexane like conformation in (II). The structures were solved using MULTAN-78 package with data collected on a CAD4-11M diffractometer and are refined to an R of 0.067 (1334 observed reflections) in (I) and an R of 0.070 (942 observed reflections) in (II). The effect of the conformational change is felt at the exocyclic substituents on phosphorus. In (I), the exocyclic oxygen and chlorine on phosphorus are in axial and equatorial positions while in (II) they are reversed. A possible intramolecular hydrogen bonding scheme is predicted for a twist-chair equilibrium.

09.3-1 STRUCTURE OF SOME ALUMINOHYDRIDE DERIVATIVES OF BISCYCLOPENTADIENYL TITANIUM.

By E.B. Lobkovsky, G.L. Soloveichik, Institute of New Chemical Problems, Chernogolovka, 142432, and A.I. Sizov, B.M. Bulychiev, Moscow State University, Moscow, 117232, USSR.

The structures of bimetallic complexes formed in Ziegler-Natta systems are of great interest because such complexes may be models of active species. We have investigated the crystal structures of three complexes formed in the catalytic system $Cp_2TiCl_2-LiAlH_4$:

$Cp_2Ti(\mu-H)_2-AlCl_2.OEt_2$ (I), $[Cp_2Ti(\mu-H)_2AlH_2]_2.Me_2N-C_2H_4NMe_2$ (II) and $[Cp_2Ti(\mu-H)_2Al(H)(\eta^1:\eta^5-C_5H_4)Ti-Cp(\mu-H)]_2$ (III). The bent sandwich moiety Cp_2-TiH_2Al

is common to all these molecules. The two bridge hydrogen atoms bonding Ti and Al atoms are in their bisectorial plane. The coordination polyhedron of the Al atom is a distorted trigonal bipyramid: $[H_2Cl_2O]$ in I, $[H_4N]$ in II and $[H_4C]$ in III. Two binuclear (Ti,Al) moieties in molecule III are bridged by the tetramethylethylenediamine molecule. In molecule III these units are joined by the intricate system of Ti-H-Al, Ti-H-Ti, Al-H-Al hydrogen bridges and bifunctional $\eta^1:\eta^5-C_5H_4$ groups. As a result, molecule III has a complex architecture with 8-membered saddle-like metal-hydride cycle $Ti-H-Al-H-Al-H-Ti-H$. The crystal structures I-III suggest wide stereochemical possibilities for a Ti-Al catalyst system.

09.3-2 THE CRYSTAL STRUCTURES OF THE ISOMERIZED γ -BUTADIENE (DICARBONYL)(ETHOXYARYLCARBENE)-IRON ORGANOMETALLIC COMPOUNDS. By You-Qi Tang, Xiang-Lin Jin and Mei-Cheng Shao, Institute of Physical Chemistry, Peking University, Beijing, Wei-Hua Xu, Jia-Bi Chen and Gui-Xin Lei, Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, China.

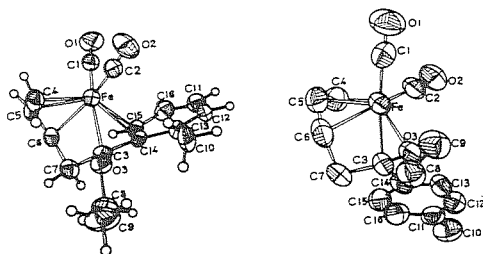
The reactions of butadiene iron tricarbonyl with para- and ortho-methyl-phenyllithium in ether at $-55^\circ C$ and subsequent alkylation by

Et_3OBF_4 in water solution at $0^\circ C$ yield two title compounds I and II with composition $C_4H_6(CO)_2FeC(OC_2H_5)C_6H_4CH_3$. After isolation and purification of the products by chromatography at low temperature, the single crystals of I and II were obtained by recrystallization from pentane solution at dry ice temperature. Both I and II are orange red with low melting point and sensitive to air and temperature. The compounds crystallize in the space group $P\bar{1}$ with $a = 8.673(3)$ Å, $b = 8.854(3)$ Å, $c = 10.977(3)$ Å, $\alpha = 91.39(2)^\circ$, $\beta = 104.52(2)^\circ$, $\gamma = 116.72(2)^\circ$, $Z = 2$, $D = 1.45$ g.cm $^{-3}$ for I and $a = 7.850(3)$ Å, $b = 10.500(5)$ Å, $c = 10.960(5)$ Å, $\alpha = 107.04(3)^\circ$, $\beta = 105.92(3)^\circ$, $\gamma = 107.01(4)^\circ$, $Z = 2$, $D = 1.37$ g.cm $^{-3}$ for II. Intensities of 1927 and 1729 unique reflections were collected with diffractometer using MoK α radiation for I and II, respectively. The structure of I was solved by direct method, while for II by Patterson-Fourier techniques. Most of the hydrogen atoms were derived from difference functions. The block diagonal least squares refinement gave final agreement factor $R_w = 0.0429$ and $R = 0.0535$ for

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I and II respectively.

The results of structure analyses show that: In reaction one π 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- π 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 π -molecular orbital composed by C14 and C15 in benzene ring 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.



(I)

(II)

to indicate Li-Li bonding. The lithium atoms are also symmetrically above and below the plane (± 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.¹ This structure is totally dissimilar to the x-ray structures of THF-solvated lithium enolates.²

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.

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

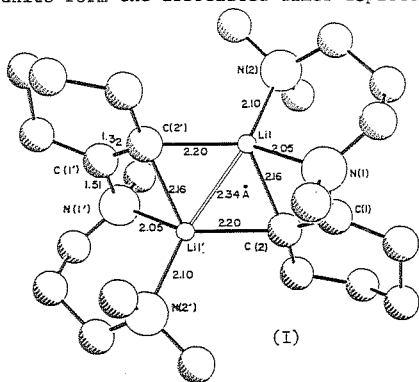
²R.Amstutz, W.B.Schweizer, D.Seebach and J.D.Dunitz, *Helv.Chem.Acta*, 1981, **64**, 2617.

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 γ_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

