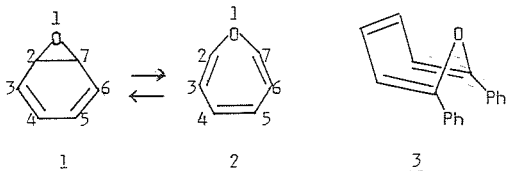


## 09.2-62 ARENE OXIDE-OXEPIN ISOMERIZATION.

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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  $3$  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.

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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  $\gamma$ -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 $\alpha$  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