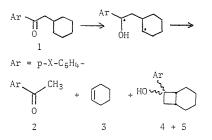
04.4 - 4MULTI-STEP CRYSTALLINE-STATE RACEMI-ZATION OF CYANOETHYL GROUP IN SOME COBALOXIME COMPLEXES. By Yasuko Tomotake, Yuji Ohashi and Yoshio Sasada, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan.

It has been found that the crystals of [(R)-1cyanoethyl](3-methylpyridine)- and [(R)-1-cya ethyl](piperidine)cobaloxime, 1 and 2 respec--1-cyanotively, reveal crystalline-state racemization with a new characteristic mode. Crystals of 1 are orthorhombic, $P2_12_12_1$, a=11.689(3), b=38.35 (2), c=9.212(2) Å at 293 K and Z=8. The unit cell was changed gradually by X-ray exposure; a=11.732, b=38.63 and c=9.332 Å after 115 h, the space group being upoltered X-ray analysis the space group being unaltered. X-ray analysis of every stage showed that only one independent molecule in an asymmetric unit, B, undergoes racemization. At 343 K, the cell dimensions of unreacted crystals are: a=11.758, b=38.52 and c =9.198 Å. X-ray irradiation at this temperature results in racemization of both of the independ-ent molecules. Change of the occupancy factors of newly developed enantiomers indicated that of newly developed enantiomers indicated that the rate of inversion of the A molecule is far slower than that of B, and that of B at room temperature is faster than at high temperature. Crystals of 2 are orthorhombic, P212121, a=11.733(2), b=31.026(5), c=11.311(2) Å and Z=8. No crystalline-state reaction was observed at 293 K. At 363 K, only one of the two independent molecules was racemized, but the change of the cell dimensions is very small. Although a reac-tion similar to 1 was expected, the crystals were broken at higher temperatures. Cavities were broken at higher temperatures. Cavities calculated for the reactive groups in the above cases well explain such complicated behaviour of reactions in these crystals.

04.4 - 5SOLID-STATE PHOTOCHEMISTRY OF α -CYCLOHEXYL-ACETOPHENONES. By Sara Ariel, V. Ramamurthy, John R. Scheffer and James Trotter, Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6

Photolysis in solution or in the solid state of α -cyclohexylacetophenones (1) yields a mixture of the corres-ponding acetophenones (2) and cyclohexene (3) [formed by bond cleavage] and the cyclobutanols 4 and 5 [formed by cyclization].



In solution the cyclobutanols are the major products; in the solid state much less cyclobutanol formation is observed. To obtain quantitative information on the mechanism of these processes, the crystal structures of la-e have been determined. All five molecules crystallize with a common conformation in which the carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring. In this

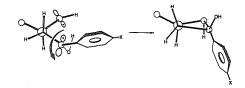
conformation the equatorial hydrogen atom H_e is favourably oriented for abstraction by oxygen via a boat-like sixatom geometry:

The O...He distances (∿ 2.6 Å)

are within the suggested upper limit of 2.72 Å (van der Waals radii sum) for this type of process. The angle τ , a measure of the displacement of the 0...H_e vector from the carbonyl plane, is in the range 42-50°

	Х	0He	τe
la	CH ₃	2.60 Å	49.6°
1b	Cl	2.60	42.0
lc	CH30	2.61	42.5
1d	COOH	2.60	43.7
1e	CN	2.65	42.1

While a coplanar arrangement (τ = 0°) is most favourable, a $cos^2\tau$ dependence for abstraction has been suggested, which in the present examples would reduce the relative reactivity by a factor of only two. The reduced amount of cyclization in the solid state can be ascribed to the fact that the formation of cyclobutanols requires extensive atomic movement, most notably large displacements of the bulky aryl groups from their original positions, a process which is topochemically unfavourable in the solid state:



04.4-6

"X-Ray Study of Some Solid State Reactions in Sn-Pb Alloys"

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Tin alloys with 0.01, 0.05 and 0.1 Pb% were prepared and homogenised by solution heat treatment in one phase region (meta -phase) for 24 houres. The alloys were plastically deformed(190%) by rolling. They were then isothermally heat treated at 170°C and 190°C in silicon oil bath for different times from 0.5 to 60 min. Both hardness and X-ray diffraction measurements were used to follow the characteristics changes. It was found that at any heating time, as the Pb% increases the hardness increases due to solid solution hardening The relation between hardness and heating time showed softening and hardening associated with different solid state reactions. Firstly, softening was observed and the hardness value reaching a minimum in less than three minutes. This is due to recrystallysation of the highly