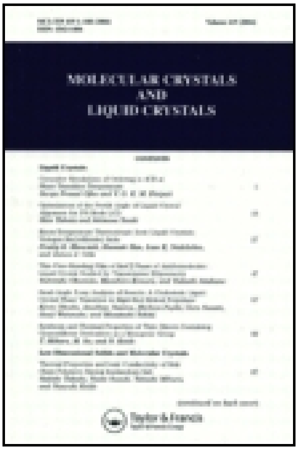

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The Molecular Rearrangement in the Solid State of an Orthocyclohexadienone into the Para Isomer

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THE MOLECULAR REARRANGEMENT IN THE SOLID STATE OF AN *ORTHO*CYCLOHEXADIENONE INTO THE *PARA* ISOMER

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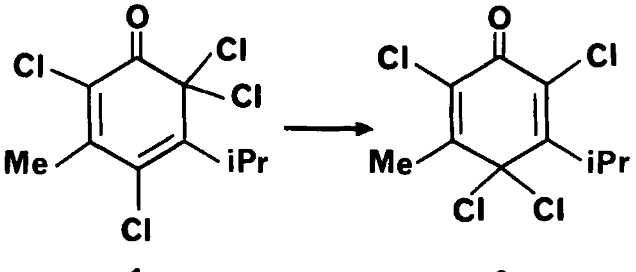
Abstract Here we describe the solid state rearrangement of orthocyclohexadienone, (1), into paracyclohexadienone, (2). The thermal and photochemical (1)→(2) transformations in the solid are homogeneous. The thermal reaction is observed to be radicalic. The observed results are rationnalized in terms of the molecular packing of crystal (1).

INTRODUCTION

Halogenocyclohexadienones are known to undergo rearrangements in the solid state. For example a tribromodienone rearranges autocatalytically and presumably homolytically in the solid phase at room temperature, giving a phenolic derivative[1]. Orthochlorocyclohexadienones have been observed to rearrange into their parachloro isomer in the solid state at room temperature and under warming[2].

We undertook this work in order to get further insight into the molecular mechanism of such transformations in the solid state. In the present paper we describe the preliminary results on the transformation in the solid state of 2,4,6,6 tetrachloro-3-methyl-5-isopropyl cyclohexa-2,4-dien-1-one, (1), into 2,4,4,6-tetrachloro-3-methyl-5-isopropyl cyclohexa-2,5-dien-1-one, (2), via a (1,3) chlorine migration.



1 2

RESULTS

After a 8 years-storage in sealed tubes crystalline compound (1), ($C_{10}H_{10}O\ Cl_4$, mp 70.5 - 71°C, monoclinic, $P2_1/c$, a = 8.398 Å, b = 11.457 Å, c = 13.274 Å, β = 108.20°, Z = 4. UV spectrum in hexane ε_{378} = 1020 ± 30) was observed to be quantitatively rearranged to crystalline product (2), ($C_{10}H_{10}O\ Cl_4$, mp 89.2 - 89,5°C, monoclinic, $P2_1/c$, a = 18.736 Å, b = 9.892 Å, c = 13.758 Å, β = 105.09°, Z = 8. UV spectrum in hexane ε_{256} = 16200 ± 500).

The solid (1) → (2) conversion can be initiated upon UV irradiation or by heating. Microscopic observations of single crystals irradiated under UV show the crystals become cloudy in the bulk. Heating solid (1) below the mp increases the (1) → (2) conversion and the reaction is accompagnied by a melt. The solid state mechanism is concluded to be homogeneous as defined in the CURTIN and PAUL paper[3]. In addition ESR signals at g = 2.007 are observed during the thermal transformation of powders and single crystals of (1). A phenoxy radical intermediate was indentified.

DISCUSSION

The molecular mechanism of the reaction is rationalized in terms of the crystalline structures of (1) and (2). Investigations of the molecular packing of compound (1) show that the distance between one chlorine atom attached to the C-6 position of a molecule of (1) and the C-4 position of the neighbouring molecule is 4.6 Å. In agreement with the topological disposition it is assumed that a radical chlorine atom migrates along the C-4 → C-6 direction. During this process two adjacent molecules (1) having their planar rings almost perpendicular move in such a way that they become nearly parallel, as they are in crystalline (2).

Such a molecular motion in the solid phase is actually under investigation.

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