Tetrahedron Letters No.1, pp. 83-84, 1970. Pergamon Press. Printed in Great Britain.

MOLECULAR STRUCTURE OF ISOPHORONE TRIMER $C_{27}H_{38}O$

E. CYROT, N. THOAI, J. WIEMANN

Laboratoire de Chimie Organique Structurale, Faculté des Sciences, Paris, France,
8 Rue Cuvier

(Received in UK 4 November 1969; accepted for publication 7 December 1969)

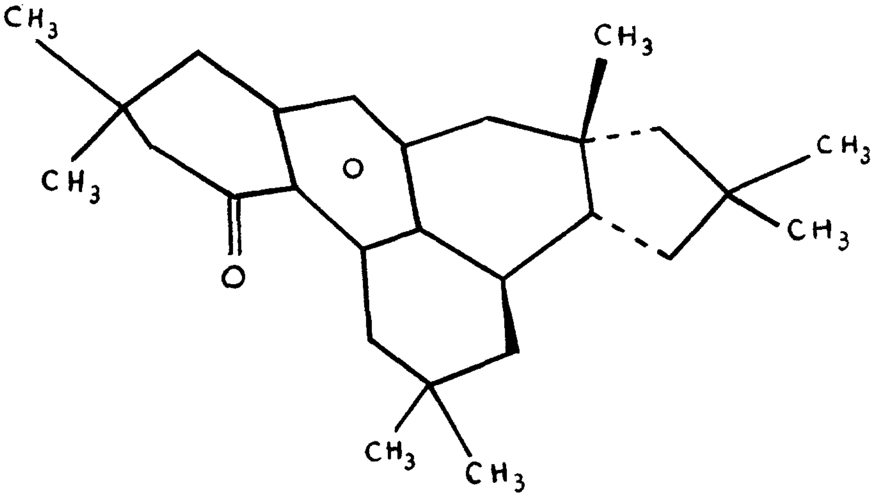
Liquid phase catalyzed condensation of methyl-3 cyclohexene-2 ones 1, such as isophorone, yields dimerized products with structures dependent on the nature of the substituents and catalyst (1)(2)(5), whereas catalyzed vapor phase condensation of isophorone leads to the unique formation of a trimer.

Magnesium oxide pellets were used as catalyst in a tubular oven heated at 300°C(3). No intermediate products of lower molecular weight, capable of giving a clue towards the structure. could be detected. Classical methods of structure elucidation (IR, Raman Spectroscopy, UV, NMR, MS) supplied interesting, yet incomplete results concerning the structure, therefore X ray diffraction remained the sole method allowing its determination with certainty. The problem was resolved by the heavy atom method. Iodation in the presence of silver trifluoroacetate (4) yields two mono-iodine derivatives, which were studied successively for the determination of crystal structure.

X ray studies did not allow structure attribution to the first iodated compound, which was the major product. The interpretation of the Weissenberg photograph for the equatorial zones proves that the lattice is monoclinic with parameters a = 15.26 Å, b = 11.53 Å, c = 14.81 Å β = 110°. The computation of Patterson's functions and the analysis of extinctions noted on the hol and hko planes indicate that the lattice spatial group is $P_{21/c}$; but certain low-intensity reflexions, forbidden by this group, are visible. Nerverthеless, computation was continued up to three-dimensional electron densities, but the carbon atoms could not be located. Thus, iodine imposes too high a degree of symmetry, which is not satisfied by the rest of the molecule.

Investigation of the molecular structure was undertaken anew with the other ono-iodated derivative. Analysis of the negatives allows the deduction of an orthorhombic lattice with parameters a = 20.62 Å, b = 19.28 Å, c = 5.96 Å.

Extinctions noted for levels hol and hko satisfy the correlations of the $P2_12_12_1$ system. Calculation of Patterson's functions confirmed this hypothesis. Five planes were recorded in the direction of the "l" axis of the crystal, allowing measurement of 617 independent reflexions.



Molecular structure of isophorone trimer

An initial calculation of three-dimensional electron densities, computed perpendicularly to the screw axis "c" resulted in localizing 16 atoms out of 29. Calculations of the structure factors with iodine and the 16 atoms, followed by the computation of electron densities, permits the attribution of the above structure for the isophorone trimer. Refinement by the least-squares method gives a reliability factor R equal 0.118.

References.

1. G. BUCHI, J.H. HANSEN, D. KNUTSON, E. KOLLER, J. Am. Chem. Soc. 80 5517(1958)
2. G. KABAS, H.C. RUTZ, Tetrahedron, 22, 1219 (1966)
3. J.J. GODFROID, Bull. Soc. Chim. 2943 (1964)
4. A.L. HENNE, W.F. ZIMMER, J. Am. Chem. Soc. 73, 1362 (1951)
5. J.P. MORIZUR, B. FURTH, J. KOSSANYI, Bull. Soc. Chim. 1422 (1967)