Crystal and Molecular Structure of 4-Methylsulphonoxyadamantanone†

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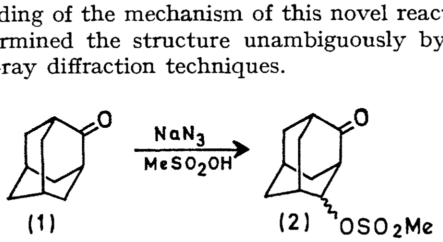
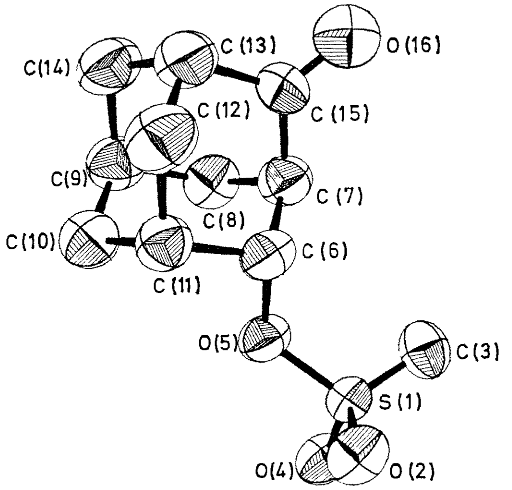
Summary The molecular structure of the title compound has been determined by single-crystal *X*-ray diffraction techniques.

THE logical attempt to expand the cyclohexanone ring of adamantanone (**1**) by a Schmidt reaction gave the unexpected product 4-methylsulphonoxyadamantanone (**2**) in high yield.[1] Unfortunately, the chemical and spectral studies that led to the formation of (**2**) did not determine the stereochemistry of the methylsulphonoxy-group. Since the stereochemistry of this product is essential for an understanding of the mechanism of this novel reaction, we have determined the structure unambiguously by single-crystal *X*-ray diffraction techniques.



Weissenberg photographs of the clear plates (from MeOH) showed that the crystals are monoclinic; $a = 12{\cdot}53 \pm 0{\cdot}01$, $b = 10{\cdot}20 \pm 0{\cdot}01$, $c = 9{\cdot}04 \pm 0{\cdot}01$ Å, and $\beta = 85{\cdot}54 \pm 0{\cdot}04°$. Systematic extinctions $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) and approximate density measurement indicated space group $P2_1/c$, $Z = 4$.



FIGURE

Most of the crystals were twinned on the (001) plane but we were able to find an untwinned crystal which was used to collect all the intensity data. Data were collected on a

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† Work was performed in the Ames Laboratory of the U.S.A.E.C.

fully automated Hilger–Watts four circle diffractometer using filtered Cu-K_α (1·5418Å) radiation. The unique reflections with $2\theta \leqslant 110°$ were corrected for background and LP factors and 1339 reflections were judged observed.

The sulphur position was determined from the three-dimensional Patterson synthesis and the 15 non-hydrogen atom positions were revealed in the subsequent sulphur-phased electron-density syntheses.[2] Full-matrix least-squares refinements in which all atomic positions and anisotropic thermal parameters were varied reduced R to its present minimum of 0·088 for the observed reflections.[3] The estimated standard deviations are ±0·01Å for bond lengths and ±1·0° for bond angles. The average C–C bond length is 1·54Å and the average C–C–C bond angle is 109·2° in this determination. The Figure is a computer drawing of the X-ray model.[4] All bond distances and angles agree well with generally accepted values. It is clear from the drawing that the methylsulphonoxy group is in an equatorial position on the cyclohexanone ring.

We thank Dr. T. Sasaki for a sample of (**2**).

(*Received, April 23rd*, 1970; *Com.* 595.)

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[3] Busing, Martin and Levy, "ORFLS: Fortran Least-Squares Program," Oak Ridge National Laboratory, USAEC, 1962.

[4] Carroll K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory, USAEC, 1965.