

The Synthesis and X-Ray Structure of
endo-7-Chloro-7-phenyl-2,5-dioxabicyclo[4.1.0]heptane

Joel D. Oliver*, James D. Woodyard, Peder E. Rush, and John R. Curtis

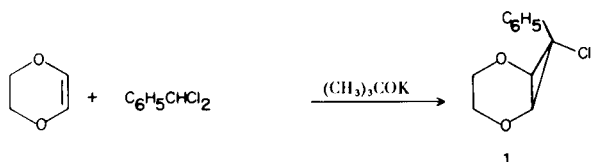
Killgore Research Center, West Texas State University, Canyon, Texas 79016

Received July 30, 1974

Sir:

As part of a continuing study of the stereochemistry of bicyclo[n.1.0]alkanes (1,2), we wish to report the synthesis and X-ray structural analysis of *endo*-7-chloro-7-phenyl-2,5-dioxabicyclo[4.1.0]heptane (**1**).

The synthesis of the title compound was accomplished by reacting benzal chloride, potassium *t*-butoxide, and dioxene (3) according to the method of Ledlie (4). This reaction afforded a 45% yield of **1**, b.p. 115-117°/3 mm,



which solidified on standing and could be crystallized from ethanol, m.p. 74-75°. Compound **1** was shown to be homogeneous by gas chromatographic analysis employing a 10% Carbowax 1500 column and was identified as one of the isomeric 7-chloro-7-phenyl-2,5-dioxabicyclo[4.1.0]heptanes on the basis of an elemental analysis consistent with the expected structure (*Anal.* Calcd. for $C_{11}H_{11}ClO_2$: C, 62.71; H, 5.26; Cl, 16.83; O, 15.19. Found: C, 62.63; H, 5.34; Cl, 17.03). Additionally, molecular ions in its mass spectrum (5) were observed at m/e 210 and 212 (3:1 ratio). Compound **1** also displays a uv absorption band (cyclohexane) at 216 nm (ϵ 9850) which has been shown to be characteristic of phenyl substituted cyclopropanes (6). The nmr spectrum of **1** furnished absorptions at 2.8-3.6 ppm (4 protons, multiplet), 3.95 ppm (2 protons, singlet), and 7.2-7.8 ppm (5 protons, multiplet). All of these data were consistent with the gross structure proposed, but they did not allow unambiguous assignment of the stereochemistry. In order to clarify the configuration at the epimeric carbon atom a single-crystal X-ray diffraction study was initiated.

Crystals of **1** from hexane are monoclinic $P2_1/n$ with $a = 5.840(1)$, $b = 16.039(1)$, $c = 10.692(1)$ Å, $\beta = 90.92(1)^\circ$, $Z = 4$. A calculated density of 1.40 g/cc for one molecule per asymmetric unit agrees favorably with the experimental density, 1.38 g/cc. Intensity data were collected on a Diano

XRD-700 diffractometer with Cu-K α radiation and with a balanced nickel-cobalt filter pair. Of the 1997 reflections measured a total of 1616 were determined to have intensities significantly above background. Phases for the structure solution were obtained by the symbolic addition procedure (7) after converting to normalized structure factor amplitudes using a K curve.

The completed structure has been refined by block-diagonal least-squares methods including anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms to a final conventional R of 0.064 (0.048 for weighted R). Refinement was considered complete when the relative change in the weighted sum of the squares of residuals, $\Sigma w(|F_o| - |F_c|)^2$, was less than 2.5% between cycles. A perspective drawing of the molecule, not including hydrogen atoms, is shown in Figure 1.

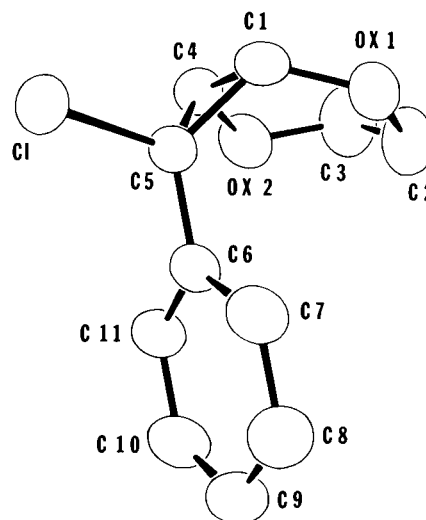


Figure 1

The structural results prove conclusively that **1** is the *endo* isomer of the expected product. The phenyleclo-

propyl moiety possesses a psuedo mirror plane, perpendicular to the phenyl ring, passing through C9, C6, C5 and bisecting the cyclopropyl ring. The atoms C1 and C4 are 1.03 and 0.98 Å, respectively, above the least-squares plane defined by the six phenyl carbon atoms, while the chlorine atom is 1.62 Å below that same plane. The six phenyl C-C distances average 1.382 ± 0.007 Å and the three cyclopropyl C-C distances average 1.511 ± 0.006 Å. These distances agree favorably with their respective accepted values. No abnormally short intermolecular contact distances were observed.

Acknowledgment.

We are grateful for the financial support of The Robert

A. Welch Foundation, under Grant Numbers AE-361 and AE-544.

REFERENCES

- (1) J. D. Woodyard, P. R. Morris, and R. G. Brownd, *J. Org. Chem.*, **37**, 4473 (1972).
- (2) P. R. Morris and J. D. Woodyard, *Org. Prep. Proced. Int.*, **5**, 275 (1973).
- (3) R. D. Moss and J. Paige, *J. Chem. Eng. Data*, **12**, 452 (1967).
- (4) D. B. Ledlie and W. H. Hearne, *Tetrahedron Letters*, 4837 (1969).
- (5) The mass spectral analysis was kindly supplied by Clifford G. Venier.
- (6) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947).
- (7) J. Karle and I. Karle, *Acta. Cryst.*, **21**, 849 (1966).