THE CRYSTAL STRUCTURE OF 2,3,6,7,7,8-HEXAMETHYL-

1,5-DIPHENYLTETRACYCLO[3.3.0.0^{2,8}.0^{3,6}]OCTAN-4-ONE

C. G. Biefeld, H. A. Eick* and H. Hart

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

The tetracyclic alcohol 1 (R=H) was recently shown[1] to ionize in FSO_3H-SO_2ClF at temp-eratures below -50° to the pyramidal cation 2[2,3] which in turn rearranges to 3[4] above -50°.


1 (R=H)   2   3
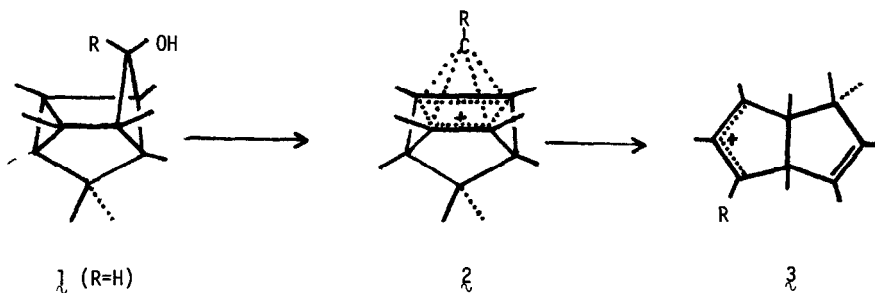
In contrast, 1 (R=CH$_3$) rearranges to 3 (R=CH$_3$) via the bicyclo[3.2.1]octadienyl cation 4[5]. The ionization 1 (R=H) → 2 clearly involves the participation of a cyclopropane bond, whereas the

1 (R=CH$_3$) ⟶   ⟶ 3 (R=CH$_3$)

4
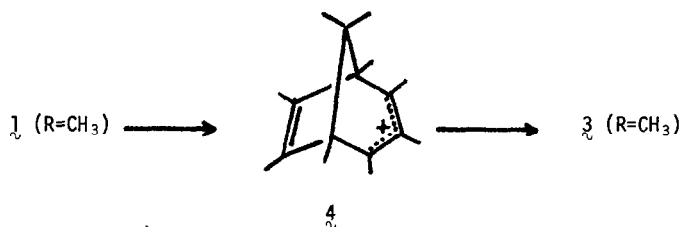
ionization of 1 (R=CH$_3$) → 4 involves in its first stages the 1,2-shift of a cyclobutane bond.

In order to understand better the chemistry of this tetracyclic ring system it seemed desirable to know its molecular parameters. Accordingly, we undertook and report here an X-ray study of the title compound 5. This representative of the ring system was selected because of
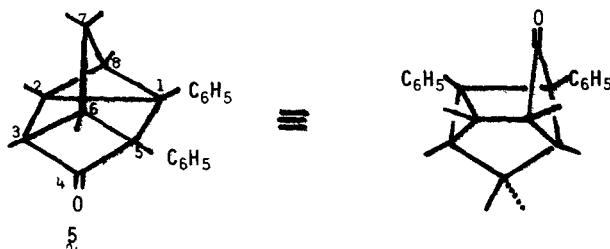
its availability [6] and because the presence of the phenyl rings could facilitate the structure
determination.

Recrystallization of 5 from petroleum ether produced clear, colorless crystals in the form
of flat plates elongated along the a-axis. Crystal data: $C_{26}H_{28}O$, M = 356.5, monoclinic, a =
9.155(3), b = 14.635(9), c = 15.425(4) Å, β = 100.7(2)°, V = 2031 Å³, Z = 4, Dm = 1.155(2), Dc =
1.166, space group uniquely $P2_1/c$ by precession techniques, MoKα monochromated radiation (λ =
0.7093 Å); Picker, four-circle, automated diffractometer, 2675 independent reflections with 1577
nonzero. A direct methods solution obtained from processing 272 normalized E's through the
program MULTAN (Main, Woolfson, Germain) produced the positions of all nonhydrogen atoms; all
hydrogen atoms were located from a difference Fourier synthesis. A full matrix refinement,
including all nonhydrogen atoms with anisotopic thermal parameters and all hydrogen atom para-
meters fixed, yielded an unweighted R = 0.082. The closest intermolecular (nonhydrogen atom)
contact, which was found to be 3.51 Å, indicates that the molecular structure is composed of
discreet molecules. Bond distances and angles are shown in the figures.
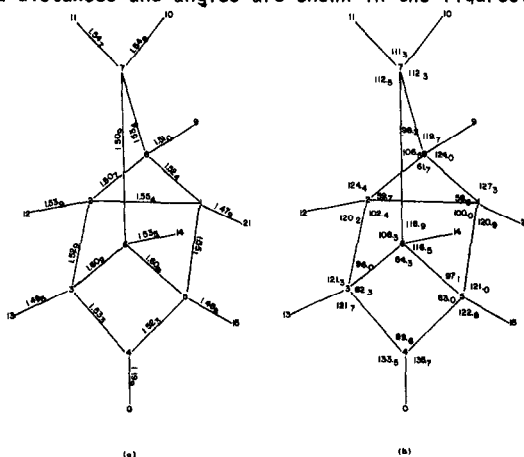

Figure 1. (a) Bond lengths (Å). Standard deviations lie in the range 0.008-0.013 Å. (b) Bond
angles (°). Standard deviations lie in the range 0.4-0.8°. Only one carbon atom of each ph
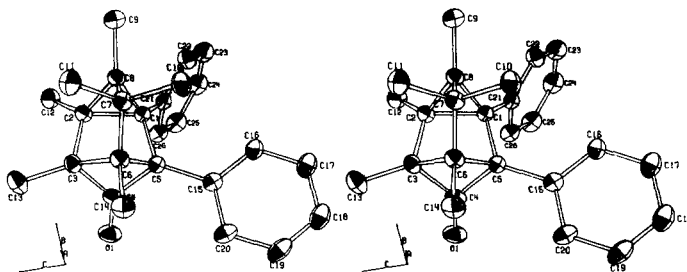is shown for simplicity (C(21) and C(15)).

Figure 2. Stereoscopic view of $\underset{\sim}{5}$ with 20% probability ellipsoids.

Two aspects of the structure are particularly significant. The distance from C4 to the midpoint of the Cl-C2 bond is only 2.145 $\overset{o}{A}$ (compared to a distance of 2.33 $\overset{o}{A}$ in a related compound[7])facilitating participation of the Cl-C2 bond in the ionization of $\underset{\sim}{1}$ (R=H) → $\underset{\sim}{2}$. The bond distances C3-C6 (1.602 (10) $\overset{o}{A}$) and C5-C6 (1.608 (8) $\overset{o}{A}$) are exceptionally long, even for a cyclobutane ring (1.548 $\overset{o}{A}$ in cyclobutane[8]). It is one of these bonds which shifts during the ionization $\underset{\sim}{1}$ (R=CH$_3$) → $\underset{\sim}{4}$. The particular path taken by $\underset{\sim}{1}$ during ionization undoubtedly depends upon the electron demand at C4; when $\underset{\sim}{1}$ is secondary and the demand is greatest, it is met by the electrons of the Cl-C2 bond, whereas when $\underset{\sim}{1}$ is tertiary the demand for participation is less, and rearrangement of the long cyclobutane bond occurs.

The remaining bond lengths do not deviate significantly from their normal values,[9-11] with the exception of C3-C13 (1.495 (9) $\overset{o}{A}$) which is shorter than the normal value of 1.537 (5) $\overset{o}{A}$.[11] Since there are few deviations in the bond lengths, the strain present in the tetracyclic system must be reflected in the small endocyclic angles with the accompanying opening of certain of the angles involving the extracyclic groups, these angles being much larger than predicted (ca. 116°[12]). The bridgehead angle of 98.2 (5)^{o} compares favorably with those in other norbornyl derivatives.[13] The cyclobutane ring is puckered with a dihedral angle of 133°, slightly smaller

than that found for other such rings.[9,14]

REFERENCES

1. H. Hart and M. Kuzuya, J. Amer. Chem. Soc., 94, 8958 (1972).

2. $(CH)_5^+$ ions were first predicted to be stable in a pyramidal geometry by W.-D. Stohrer and R. Hoffmann, J. Amer. Chem. Soc., 94, 1661 (1972).

3. For other examples of $(CH)_5^+$ - type ions, see (a) S. Masamune, M. Sakai, H. Ona and A. J. Jones, J. Amer. Chem. Soc., 94, 8956 (1972); (b) H. Hogeveen and P. W. Kwant, Tetrahedron Lett., 1665 (1973); R. K. Lustgarten, J. Amer. Chem. Soc., 94, 7602 (1972). For a related $(C_{11}H_{11})^+$ cation, see M. J. Goldstein and S. A. Kline, J. Amer. Chem. Soc., 95, 935 (1973).

4. M. Kuzuya and H. Hart, Tetrahedron Lett., manuscript submitted.

5. H. Hart and M. Kuzuya, J. Amer. Chem. Soc., 95, 4096 (1973); M. Kuzuya and H. Hart Tetrahedron Lett., in press.

6. H. Hart and G. M. Love, J. Amer. Chem. Soc., 93, 6266 (1971).

7. S. Masamune, R. Vukov, M. J. Bennett, and J. T. Purdham, J. Amer. Chem. Soc., 94, 8239 (1972)

8. A. Almenningen, O. Bastiansen, and P. N. Skancke, Acta Chem. Scand., 15, 711 (1961).

9. E. Adman and T. N. Margulis, J. Amer. Chem. Soc., 90, 4517 (1968).

10. A. Hartman and F. L. Hirshfeld, Acta Crystallogr., 20, 80 (1966).

11. L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement 1956-1959," The Chemical Society, London, 1965.

12. M. Yu Lukina, Russ. Chem. Rev., 31, 419 (1962).

13. C. Altona and M. Sundaralingam, Acta Crystallogr., B28, 1806 (1972).

14. Full structural details will be published elsewhere.