Acta Chemica Scandinavica B 31 (1977) 387—390

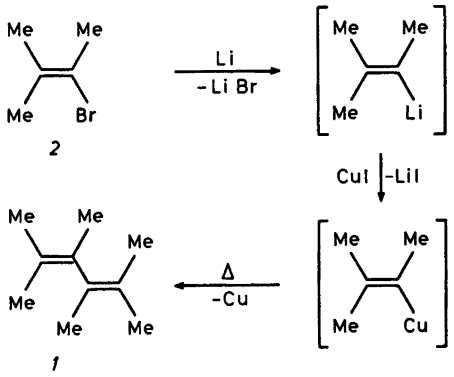
Synthesis and Molecular Structure of 2,3,4,5-Tetramethyl-2,4-hexadiene

MARIT TRÆTTEBERG [a] and LEIV KR. SYDNES [b]

[a] Department of Chemistry, University of Trondheim, NLHT, N-7000 Trondheim, Norway and
[b] Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

2,3,4,5-Tetramethyl-2,4-hexadiene (*1*) has been prepared in 23 % yield from 2-bromo-3-methyl-2-butene in a two-step synthesis. The molecular structure of *1* has been determined. The molecule was found to have *gauche* conformation.

2,3,4,5-Tetramethyl-2,4-hexadiene (*1*) was first isolated in 1955 by Braude and Evans [1] as a by-product (< 7 %) in the preparation of 1,2-dimethyl-1-propenyllithium from 2-bromo-3-methyl-2-butene (*2*). Later two synthetic pathways to this diene have been published. Criegee *et al.*[2] isolated *1* in 18 % overall yield in a five-step synthesis starting from 2-butyne and dimethylmaleic anhydride, while Forbes *et al.*[3] prepared the compound from 2-methyl-2-butene as starting material. For a number of reasons we found the last procedures unsatisfactory, and we therefore turned our attention to the original observation of Braude and Evans.



Scheme 1.

It has been shown recently that coupling of vinylic lithium [4] and Grignard [5] derivatives by means of copper(I) salts give the corresponding dienes in good yields, and this procedure was attempted for the preparation of diene *1*. The bromide *2* was converted into the corresponding lithium or Grignard derivative and either copper(I) chloride, copper(I) iodide or tetrakis[iodo(tributylphosphine)copper(I)] was used as coupling reagent. In all cases pure *1* was isolated, but the yields varied with the reagents used, being highest (23 %) from the reaction of the lithium derivative and cuprous iodide (Scheme 1).

The molecular structure of 2,3,4,5-tetramethyl-2,4-hexadiene poses interesting problems. Conjugated dienes show a strong preference for assuming an *s-trans* conformation, but because of the steric requirements of the methyl groups an *s-trans* conformation is energetically unfavourable for *1*. The determination of the preferred conformation of *1* is therefore of great interest. The obtained results are expected to contribute to elucidating the torsional potential energy of $C_{sp^2}-C_{sp^2}$ bonds.

EXPERIMENTAL

Preparation of 2,3,4,5-tetramethyl-2,4-hexadiene (1). Under a nitrogen atmosphere a solution of 75.0 g (0.50 mol) of 3-bromo-2-methyl-2-butene (*2*) [6] in 150 ml of dry ether was added to 7.8 g (1.13 mol) of finely cut lithium (0.9 % sodium) in 600 ml of dry ether with vigorous stirring and cooling (ice/water). After 20 h of stirring at 40 °C unreacted lithium was filtered off and the filtrate was added dropwise during

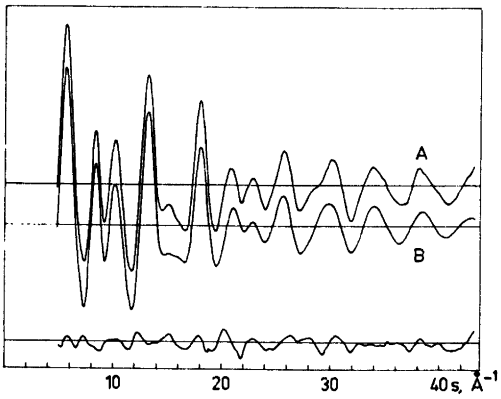


Fig. 1. Experimental (A) and theoretical (B) molecular intensity functions of *1* and the difference between the two.

1½ h to a suspension of 124.0 g (0.65 mol) of anhydrous cuprous iodide in 800 ml of dry ether kept at −60 °C (CO_2/acetone). After addition was complete the greyish mixture was stirred for 1 h at this temperature, then allowed to attain room temperature overnight, and finally heated with reflux for 2 h. 300 ml of 0.3 N HCl was added, the inorganic salts were removed by filtration, and the product was extracted with ether and dried ($MgSO_4$). Evaporation of the ether and fractionation of the residue through a spinning-band column gave 8.0 g (23 %) of *1* b.p. 73.5 °C (60 mmHg); n_D^{24} 1.4500 (lit.[3] b.p. 143–144 °C; n_D^{24} 1.4486); gas chromatography showed a purity of better than 98.5 %. The spectroscopic data are in accordance with those published.[2]

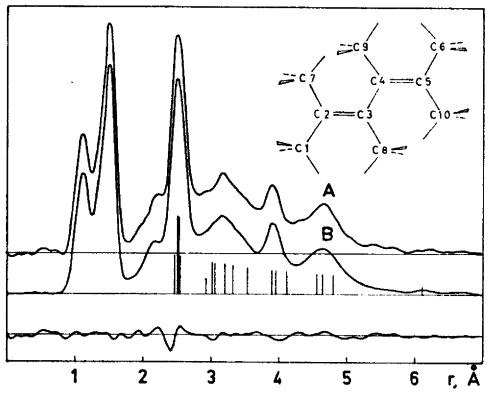


Fig. 2. Experimental (A) and theoretical (B) radial distribution functions of *1*, and the differences between the two. Artificial damping constant k = 0.0012.

Electron diffraction experiment. The electron diffraction data of *1* were collected with the Oslo Apparatus.[7] Two sets of photographic plates were recorded at nozzle-to-plate distances of 480.71 and 200.71 mm, respectively. Both sets were recorded at room temperature and at an electron wavelength of 0.064628 Å. From the two sets of data 5, respectively 4, plates were selected for further use. The data were treated in the usual way using the modification function $s/|f_C'|^2$.[8] Two average intensity curves were computed, one from each set of the data. The curves covered the s intervals 1.50 – 19.25 and 7.00 – 43.25 Å^{-1} with Δs values of 0.125 and 0.250 Å^{-1}, respectively. Finally a composite intensity curve was computed (see Fig. 1).

The experimental radial distribution (RD) curve [8] calculated by Fourier inversion of the composite intensity curve is shown in Fig. 2. The molecular structure of the title compound was determined by least squares refinements of the molecular intensities.

STRUCTURAL ANALYSIS

The molecular model that was used in the least squares refinements, was based on the following assumptions:

1. coplanar bonds around each of the CC double bonds;

2. local C_{3v} symmetry at each of the methyl groups;

3. the symmetry axis of each of the methyl groups coinciding with the adjoining CC bond;

4. one of the hydrogen atoms of each methyl group coplanar with the nearest CC double bond [$\omega(=C-C-H)=0°$].

The first two assumptions are reasonable. The latter two are probably not justified to the same extent, as the methyl groups in *cis*-2-butene [9] were found to be tilted away from the double bond (4.9°) and also rotated (9.0°) about the adjacent C – C bonds in such a way as to increase the distance between the two crowded hydrogen atoms. In the present case it was not possible to determine the tilt and rotation parameters of the methyl groups because of the larger complexity of this molecule. As the error limits of the tilt and rotational parameters determined for *cis*-2-butene were quite large and of the same order of magnitude as the observed deviations from the conditions inherent in assumptions 3 and 4, it was decided to use these in the present case. They will, however, hardly affect the determination of the carbon skeletal structure.

With the assumptions given above the geometry of *1* is determined by ten parameters. These are the four different bond distances (=C–C=, C=C, C–CH_3 and C–H), five bond angles ($\angle C_1-C_2=C_3$, $\angle C_2=C_3-C_8$, $\angle C_2=C_3-C_4$, $\angle C_3=C_2-C_7$, $\angle C-C-H$, see Fig. 2 for the numbering of atoms) and the dihedral angle of the central CC bond, $\omega(C_3-C_4)$.

By studying the experimental RD function it was fairly easy to rule out a molecular model of *1* with a planar carbon skeleton. The internuclear distances of a molecular model corresponding to *s-gauche* conformation fitted, however, quite well to the various peaks of the experimental RD-curve.

It was not possible to vary all CCC valence angles simultaneously in the least squares refinements. One valence angle was therefore kept constant during one run, but was varied systematically over the expected range. The value corresponding to the lowest squared error sum was then used for this angle parameter. As the angles $\angle C_2=C_3-C_8$ and $\angle C_3=C_2-C_7$ were found to be very similar, they were set equal in the latter part of this investigation.

Only a few of the vibrational amplitudes (u) could be refined together with the geometrical parameters. The other u values were either kept at the calculated values or adjusted somewhat based on the shape of the peaks in the RD-curve.

The RD-curve corresponding to the best molecular model determined by least squares refinements of the intensities showed obvious shrinkage effects when the dependent distances were based on an r_a structure. Especially the peak at 3.9 Å (C_3C_6 and C_7C_8) was clearly displaced to larger r-values in the theoretical RD-curve compared to the experimental one. These effects did, however, vanish when an r_α structure was studied, as will be seen from Fig. 2, which shows the experimental RD-curve together with the corresponding theoretical curve based on the best r_α structure. The mean vibrational amplitudes and the correction coefficients necessary to determine an r_α structure were calculated as described by Stølevik *et al.*,[11] using Allinger's force constants.[12]

The structural parameters determined for *1* are presented in Table 1. Table 2 gives the non-bonded carbon carbon distances together with the vibrational amplitudes that were used in the least squares analyses (u^{ED}) as well as those calculated (u^{calc}). Fig. 2 shows the numbering of the atoms in *1*, which is used in the present study. For the sake of convenience the model is shown with *s-trans* conformation.

DISCUSSION

The most important parameter in the 2,3,4,5-tetramethyl-2,4-hexadiene molecular structure is the C_3-C_4 dihedral angle, which determines the overall comformation of the molecule. It is well known that conjugated CC double bonds have a strong preference for assuming *s-trans* conformations wherever this is possible. In the present case an *s-trans* conformation is expected to be energetically unfavourable because of serious sterical interference between pairs of methyl groups. The C_3-C_4 dihedral angle is determined to be 60.0°, corresponding to *s-gauche*

Table 1. Geometrical parameters and vibrational amplitudes for 2,3,4,5-tetramethyl-2,4-hexadiene as determined from least squares refinements. The numbers in parentheses are standard deviation values from the least squares analyses. The bond distances are given as r_a values.

Distances	r_a (Å)	u (Å)	Angles	(°)
=C–C=	1.487 [a]	0.050	$\angle C_1-C_2=C_3$	125.2 [a]
–C=C–	1.349(2)	0.041(3)	$\angle C_2=C_3-C_8$	123.6(2)
=C–C–	1.515(1)	0.056(1)	$\angle C_2=C_3-C_4$	125.0(2)
C–H	1.117(2)	0.087(3)	$\angle C_3=C_2-C_7$	123.6 [b]
			$\angle C-C-H$	110.5(1)
			$\omega(C_3-C_4)$	60.0(<1)

[a] Determined by the combined trial and error/least squares method described in the text. [b] Assumed equal to $\angle C_2=C_3-C_8$.

Table 2. Non-bonded carbon carbon distances and the corresponding mean amplitudes of vibration.

	r_a (Å)	u^{ED} (Å)	u^{calc} (Å)
C_3C_9	2.459		0.0878
C_3C_5	2.493		0.0749
C_1C_7	2.503	0.0795[a](67)	0.0893
C_8C_7	2.543		0.0763
C_1C_3	2.516		0.0753
C_8C_9	2.922	0.1850	0.1873
C_3C_{10}	3.053	0.1550	0.1553
C_7C_{10}	3.204	0.2100	0.2115
C_1C_8	3.010	0.1530	0.1538
C_3C_5	3.202	0.1200	0.1403
C_9C_{10}	3.316	0.2000	0.2607
C_5C_9	3.529	0.1250	0.1263
C_3C_6	3.890	0.0788	0.0788
C_7C_8	3.947	0.0795	0.0795
C_7C_9	4.115	0.1860	0.1860
C_6C_7	4.553	0.2597	0.2770
C_2C_6	4.639	0.1325	0.1389
C_1C_9	4.791	0.1270	0.1366
C_1C_6	6.105	0.1302	0.1302

[a] Assumed equal.

conformation. The standard deviation of this parameter is found to be unusually small.

Similar sterical interferences between pairs of methyl groups as in *1* are encountered in the *trans, trans* and *cis, trans* isomers of 3,4-dimethyl-2,4-hexadienes.[10] These molecules were also found to have *s-gauche* conformations, but the dihedral angles were slightly larger (66.7 and 65.7°) than in *1*. The results obtained for the C_3-C_4 dihedral angle indicate that a three-fold barrier of rotation probably makes an important contribution to the torsional energy of a $C_{sp^2}-C_{sp^2}$ single bond.

The central CC single bond is found to be longer than the $C_{sp^2}-C_{sp^2}$ bond in butadiene (1.487 *vs.* 1.467 Å).[13] This effect probably reflects small differences in hybridization of the carbon atoms in the two molecules. This explanation is in accordance with the observation that the two other σ bonds directing from each of the carbon atoms under discussion makes a larger angle in *1* (123.6°) than in butadiene (119.5°).

The other bond lengths determined for *1* agree well with results obtained for structurally related molecules [14] and will not be discussed further.

The determined bond angles show that some of the strain in the molecule is relieved through enlarged valence angles at the double bonds. In *cis*-2-butene the CCC valence angle is found to be 125.4°. In the present case the C=C–C valence angles at the *cis* methyl groups are found to be 123.6°. In *1* the sterical strain is, however, substantial also on the other side of the double bond, and it will be seen that the CCC valence angles are slightly larger on this side (125°). The differences between the various valence angles at the double bonds are fairly small and the angles can hardly be claimed to be significantly different, even if the standard deviations of those angles that are varied in the least squares refinements are unusually small.

Acknowledgement. The authors want to thank cand. real. Arne Almenningen for making the electron diffraction diagrams and ing. Pirkko Bakken for helpful assistance in the structure determination. Financial support from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

REFERENCES

1. Braude, E. A. and Evans, E. A. *J. Chem. Soc.* (1955) 3331.
2. Criegee, R., Zirngibl, U., Furrer, H., Seebach, D. and Freund, G. *Chem. Ber. 97* (1964) 2942.
3. Forbes, W. F., Shilton, R. and Balasubramanian, A. *J. Org. Chem. 29* (1964) 3527.
4. Whitesides, G. M., Casey, C. F. and Krieger, J. K. *J. Am. Chem. Soc. 93* (1971) 1379.
5. Kauffmann, T. and Sahm, W. *Angew. Chem. 79* (1967) 101.
6. Böeseken, J. *Recl. Trav. Chim. Pays-Bas 54* (1935) 657.
7. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand. 9* (1955) 232.
8. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand. 23* (1969) 3224.
9. Almenningen, A., Anfinsen, I. M. and Haaland, A. *Acta Chem. Scand. 24* (1970) 43.
10. Trætteberg, M. *Acta Chem. Scand. 24* (1970) 2295.
11. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett. 15* (1972) 263.
12. Allinger, N. L. and Sprague, J. T. *J. Am. Chem. Soc. 94* (1972) 5734.
13. Trætteberg, M. *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967.
14. Kuchitsu, K. In Allen, G., Ed., *MTP Int. Rev. Science*, Butterworth, Oxford 1972.

Received December 13, 1976.