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TETRAISOPROPYLETHYLENE

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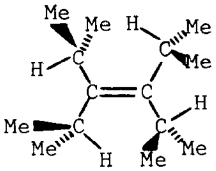
As part of our continuing program[1] for the investigation of crowded alkenes, tetraisopropylethylene (1) was an attractive goal for study. We predicted this molecule would prefer the conformation shown to minimize the steric interactions, and recent force field calculations support this geometry.[2] In this structure the methine hydrogens of the isopropyl groups would exist in two pairs in the plane of the double bond, with one pair near the axis of the double bond, and the other pair alongside the double bond. These pairs could be interconverted by a synchronous rotation around all four of the single bonds to the double bond.



1

We have now prepared tetraisopropylethylene, and its spectral properties support the structural proposal made for this compound.

The McMurry olefin synthesis (eq. 1)[3] gave 1 as white needles in 6% yield : mp 116-117°; mass spectrum (70 eV) m/e (relative intensity) 196 (M^+, 6), 98 (12), 83 (100), 55 (16), and 43 (13); UV (hexane) 204 nm (ε 7000).

$$\underline{i}\text{-Pr}_2\text{C=O} \xrightarrow{\text{Ti(II)}} \underbrace{\underline{i}\text{-Pr}_2\text{-C=C-}\underline{i}\text{-Pr}_2}_{1} \qquad (1)$$

The nmr spectrum of 1 was temperature dependent (see Figure 1). At 2.5° two isopropyl doublets of equal intensity were observed, at δ 0.91 and 1.10, and two methine heptets of equal intensity were centered at δ 2.28 and 2.94. At 35° the pairs of signals were undergoing coalescence, and at 61° a single sharp isopropyl doublet (J = 7 Hz) at δ 1.00 was visible, along with a single multiplet at δ 2.6. The appearance of two distinct pairs of isopropyl groups is what was anticipated for the predicted geometry. Other conformations, including one with both methyls of an isopropyl on the same side of the plane of the double bond, would be expected to show greater multiplicity.

The unique conformational properties of the isopropyl group have previously resulted in similar locked conformations in hexaisopropylbenzene,[4] and the triisopropylmentyl radical.[5] Recent studies have also appeared of compounds with two adjacent isopropyl groups where conformational isomerism can be observed.[6,7] The coupled rotation of such groups as observed by nmr has been designated as the "gear effect",[6] or the "cogwheel effect."[8]

The number of methods available for the preparation of olefins has recently been increasing rapidly.[2,9] The use of these new techniques, as well as others already known, has led to syntheses of a number of interesting strained olefins, particularly those with bridgehead double bonds.[10] It is anticipated that other unique olefins will be accessible and we are actively pursuing their preparation.

It is also worthy of note that tetracyclopropylethylene has been prepared but no conformational isomerism was reported for the compound,[11] perhaps because of the complexity of its nmr spectrum.

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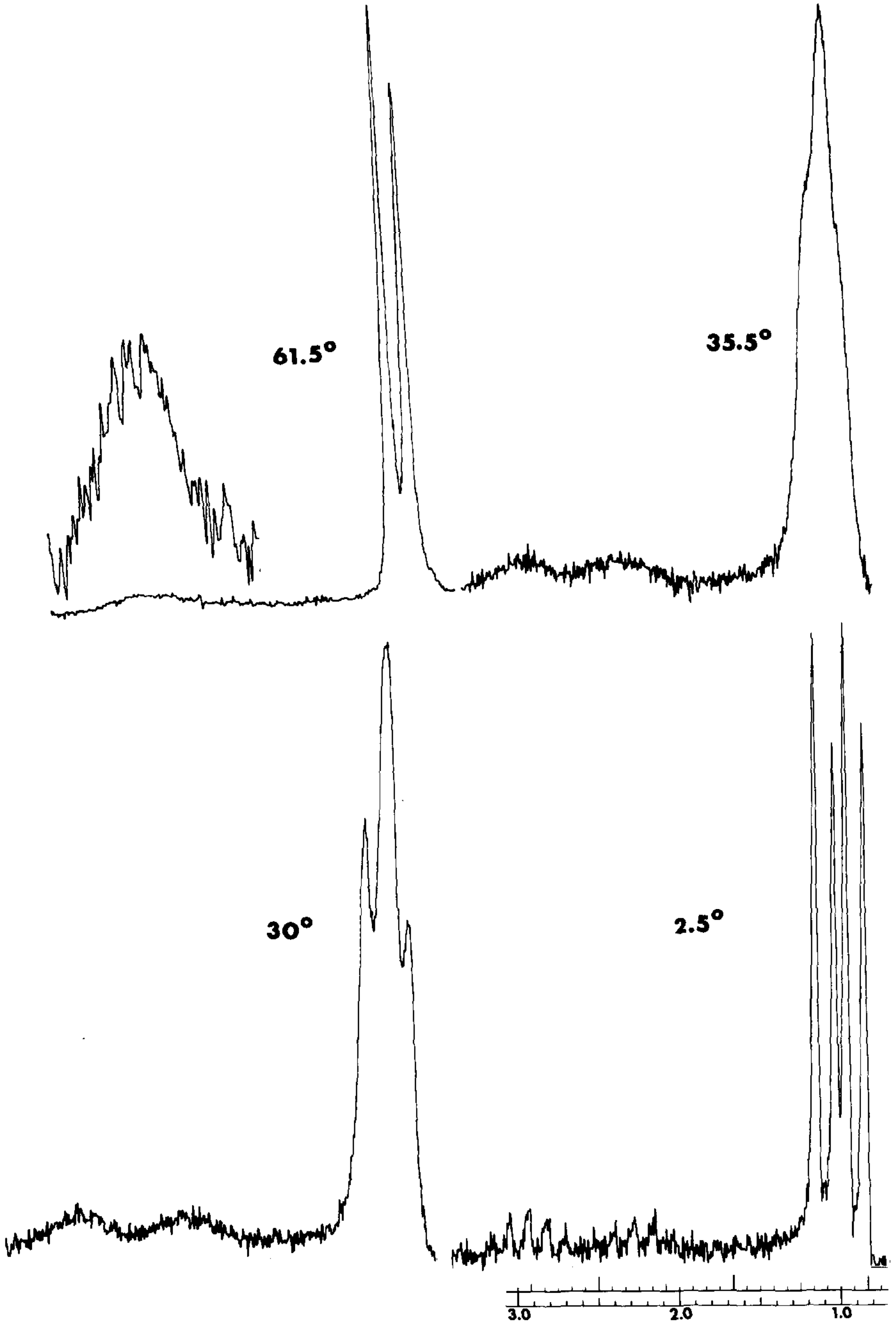

Figure 1. Temperature Dependence of the NMR Spectrum of Tetraisopropylethylene (60 MHz).

References

(1) G.J. Abruscato and T.T. Tidwell, *J. Org. Chem.*, **37**, 4151 (1972); *J. Amer. Chem. Soc.*, **92**, 4125 (1970).

(2) O. Ermer and S. Lifson, *Tetrahedron*, **30**, 2425 (1974).

(3) (a) J.E. McMurry, *Accounts Chem. Res.*, **7**, 281 (1974);
(b) J.E. McMurry and M.P. Fleming, *J. Amer. Chem. Soc.*, **96**, 4708 (1974).

(4) E. M. Arnett and J.M. Bollinger, *J. Amer. Chem. Soc.*, **86**, 4729 (1964).

(5) D. Griller, S. Icli, C. Thankachan, and T.T. Tidwell, *J. Chem. Soc., Chem. Commun.*, 931 (1974).

(6) A. Lidén, C. Roussel, M. Chanon, J. Metzger and J. Sandström, *Tetrahedron Lett.*, 3629 (1974).

(7) D.S. Bomse and T.H. Morton, *Tetrahedron Lett.*, 3491 (1974).

(8) H. Kwart and S. Alekman, *J. Amer. Chem. Soc.*, **90**, 4482 (1968).

(9) (a) N. Kornblum, S.D. Boyd, H.W. Pinnick, and R.G. Smith, *J. Amer. Chem. Soc.*, **93**, 4316 (1971); (b) D.J. Faulkner, *Synthesis*, 175 (1971); (c) A.P. Krapcho and E.G.E. Jahngen, Jr., *J. Org. Chem.*, **39**, 1650 (1974); (d) K.B. Sharpless and T.C. Flood, *Chem. Commun.*, 370 (1972); (e) N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, *Tetrahedron Lett.*, 2961 (1974); (f) D.H.R. Barton, F.S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin I*, 1794 (1974); (g) J-J. Katz, B.A. Carlson, and H.C. Brown, *J. Org. Chem.*, **39**, 2817 (1974); (h) J.S. Grossert, J. Buter, E.W.H. Asveld, and R.M. Kellogg, *Tetrahedron Lett.*, 2805 (1974).

(10) (a) R.L. Viavattene, F.D. Greene, L.D. Cheung, R. Majeste, and L.M. Trefonas, *J. Amer. Chem. Soc.*, **96**, 4342 (1974); (b) B.L. Adams and P. Kovacic, *ibid.*, **96**, 7104 (1974); (c) A.H. Alberts, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 543, 3047 (1973); (d) D. Lenoir, *ibid.*, 4049 (1972); (e) A.D. Wolf and M. Jones, Jr., *J. Amer. Chem. Soc.*, **95**, 8209 (1973); (f) J.E. Gano and L. Eizenberg, *ibid.*, **95**, 972 (1973); (g) W.G. Dauben and J. Ipaktschi, *ibid.*, **95**, 5088 (1973); (h) M. Farcasiu, R.T. Conlin, M. Jones, Jr., and P. v. R. Schleyer, *ibid.*, **95**, 8207 (1973); (i) H. H. Grootveld, C. Blomberg, and F. Bickelhaupt, *Chem. Commun.*, 542 (1973); (j) G. Köbrich, *Angew. Chem. Inter. Ed. Engl.*, **12**, 464 (1973).

(11) (a) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc., C.*, 3252 (1971); (b) A. Nierth, H. M. Ensslin, and M. Hanack, *Annalen*, **733**, 187 (1970).