

mixture of their diacid precursors with trifluoroacetic anhydride, distilling off **15**, the anhydride product; **15** was converted into **13** with methanol followed by diazomethane, while esterification of the distillation residue yielded **14**.

Clearly, TFS dimerizes in the same head-to-head fashion as many perhalogenated fluoroolefins. A number of its cycloadditions have been investigated and will be reported in forthcoming publications.

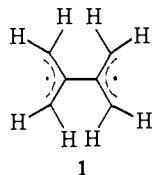
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Tetramethyleneethanes. Preparation and Reactions of a Stereochemically Labeled Precursor

Sir:

Tetramethyleneethane (**1**) and its derivatives could



well be intermediates in the dimerization of allenes to 1,2-dimethylenecyclobutanes¹ and also in thermally induced rearrangements of the latter.² At low temperatures a triplet state of **1** is observed by esr spectroscopy,³ derivatives of **1** appear to have been intercepted by chemical reaction.^{1b,2d,4} Speculations, based on both theory and experimentation, have been made concerning the geometry and nature of bonding in **1** and the stereochemistry of the conceivable reactions by which it may annihilate itself forming stable products.⁵

(1) (a) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); (b) T. L. Jacobs and R. C. Kammerer, *J. Amer. Chem. Soc.*, **94**, 7190 (1972), and earlier references; (c) W. R. Moore, R. D. Bach, and T. M. Ozretich, *ibid.*, **91**, 5918 (1969); (d) W. R. Roth, M. Heiber, and G. Erker, *Angew. Chem.*, **85**, 511 (1973); (e) E. V. Dehmlow and G. C. Ezimora, *Tetrahedron Lett.*, 1265 (1972); (f) review J. E. Baldwin and R. H. Fleming, *Fortsch. Chem. Forsch.*, **15**, 281 (1970).

(2) (a) W. von E. Doering and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **89**, 4534 (1967); (b) J. J. Gajewski and C. N. Shih, *ibid.*, **94**, 1675 (1972); (c) W. R. Dolbier, Jr., and S-H. Dai, *ibid.*, **92**, 1774 (1970); (d) C-S. Chang and N. L. Bauld, *ibid.*, **94**, 7593 (1972); N. L. Bauld and C-S. Chang, *ibid.*, **94**, 7594 (1972); (e) see also W. R. Roth and G. Erker, *Angew. Chem.*, **85**, 512 (1973); W. Grimme and H-J. Rother, *ibid.*, **85**, 512 (1973); (f) for corresponding anion radicals see N. L. Bauld and G. R. Stevenson, *J. Amer. Chem. Soc.*, **91**, 3675 (1969).

(3) P. Dowd, *J. Amer. Chem. Soc.*, **92**, 1066 (1970).

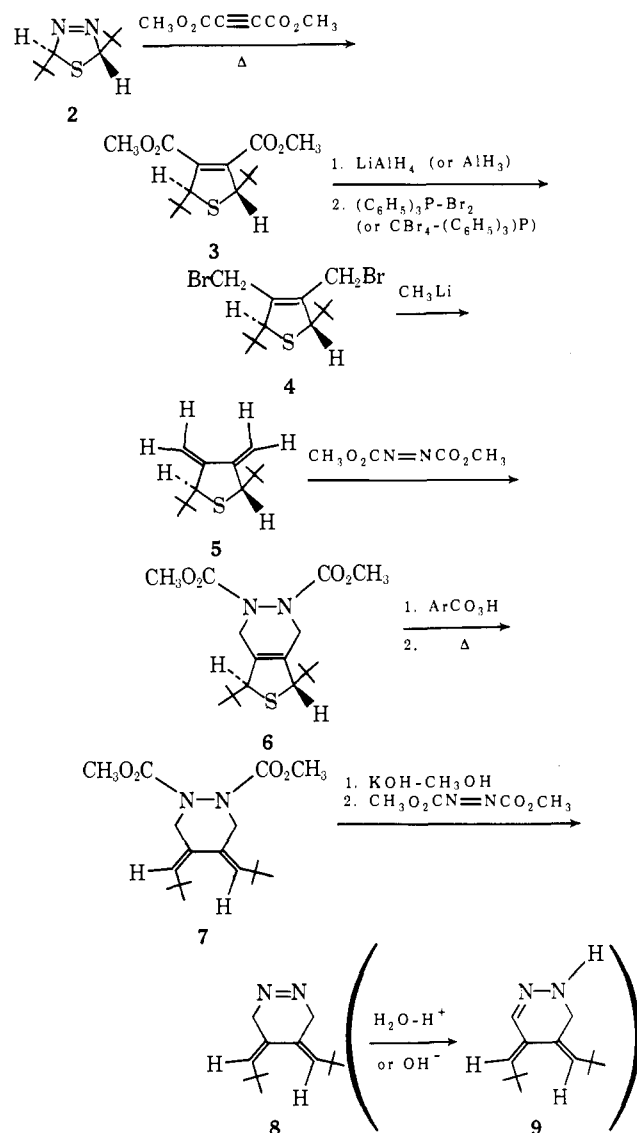
(4) (a) A. Nakamura, *Bull. Chem. Soc. Jap.*, **39**, 543 (1966); (b) R. Ben-Shoshan and R. Pettit, *Chem. Commun.*, 247 (1968); R. E. Davis, *ibid.*, 248 (1968).

(5) Especially B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970) and ref 1f; also W. W. Schoeller, *Tetrahedron Lett.*, 2043, 2047 (1973).

A reasonable route to tetramethyleneethanes would be through decomposition of an appropriate azo precursor. We describe here the synthesis and thermal reactions of such a precursor, labeled stereochemically with *tert*-butyl groups at two carbon atoms. The synthetic method has potential generality.

Scheme I shows the approach. Reduction and bro-

Scheme I



mination of **3**⁶ provide dibromide **4** (overall 70%), which with methyl lithium⁷ gives in 77% yield *trans*-2,5-di-*tert*-butyl-3,4-dimethylenethiolane (**5**) (nmr (CCl_4) δ 0.90 (s, 18, *t*-Bu), 3.50 (br s, 2,2,5-H), 4.76 (br s, 2, vinyl H), and 5.25 (br s, 2, vinyl H)). The first representative of this compound class was reported concurrently with this work.⁸ Cycloaddition with dimethyl azodicarboxylate gives **6** (88%), which on

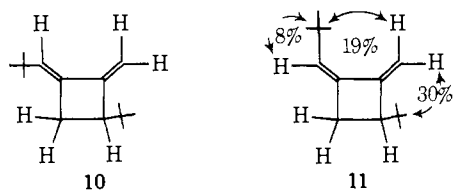
(6) J. Buter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, **37**, 4045 (1972).

(7) Methyl lithium was prepared from methyl iodide to a product containing strongly complexed iodine.

(8) S. Sadeh and Y. Gaoni, *Tetrahedron Lett.*, 2365 (1973); for an early unsuccessful attempt to prepare these compounds see C. S. Marvel, R. M. Nowak, and J. Economy, *J. Amer. Chem. Soc.*, **78**, 6171 (1956). We have prepared other derivatives of 3,4-dimethylenethiolane using the route described here.

oxidation to the sulfone with *m*-chloroperbenzoic acid (ArCO₃H) followed by pyrolysis⁹ affords exclusively **7** (overall 83%). Hydrolysis-decarboxylation using the excellent method of Kopecky and Evani¹⁰ gave a hydrazine derivative (not isolated) that was dehydrogenated to **8** using dimethyl azodicarboxylate as hydrogen acceptor.¹¹ The overall yield was 100% determined by nmr. Even trace amounts of water catalyze rapid tautomerization to **9**. Solutions of **8** must be prepared under rigorously dry and oxygen-free conditions. In the pmr spectrum (C₆D₆) **8** displays δ 1.00 (s, 9, *t*-Bu), 1.03 (s, 9, *t*-Bu), 4.52 (br s, 2, CH₂), 4.99 (br s, 2, CH₂), 5.10 (br s, 1, vinyl H), and 5.33 (br s, 1, vinyl H).

As a 0.1 *M* solution in hydrocarbon solvent **8** is completely decomposed within 240 sec at 190°. A mixture of two isomeric (C₁₄H₂₄, **8** less N₂) compounds, **10** and **11**, is formed in 85 ± 5% yield (glpc analysis).¹²



After 240 sec the ratio of **10** to **11** is about 1:4 but **11** is thermally unstable and rearranges to **10** on further pyrolysis; **10** eventually becomes virtually the only product.¹³ Pure **10** has 100-MHz nmr (C₆D₆): δ 0.93 (s, 9, *t*-Bu), 1.06 (s, 9, *t*-Bu), 2.57–2.68 (complex absorption, 3, ring H), 4.77 (d, *J* = 1.5 Hz, 1, vinyl H), 5.24 (d, *J* = 2.2 Hz, 1, vinyl H), and 5.68 (d of d, *J* = 2.0, 2.5 Hz, 1, vinyl H); uv (C₂H₅OH) λ_{\max} 256 nm (ϵ 17,000). These data uniquely describe **10** as being 3-*tert*-butyl-2-methylene-*anti*-neopentylidene-cyclobutane.¹⁴ The anti configurational assignment rests on the normal value for the ultraviolet absorption indicating the absence of unusual steric distortion.

To demonstrate that **11** is the primary thermolysis product, a sample of *neat* **8** was pyrolyzed at 190°. The volatile product distilled immediately from the reaction mixture was at least 95% pure **11** (considerable polymer forms also). No **10** was detectable in the distillate. Compound **11** has 100-MHz nmr (C₆D₆): δ 0.91 (s, 9, *t*-Bu), 1.18 (s, 9, *t*-Bu), 2.08–2.70 (complex absorption, 3, ring H), 5.02 (complex t, 1, vinyl H), 5.26 (complex m, 1, vinyl H), and 5.33 (complex d, 1, vinyl H); there is no uv absorption above 220 nm.¹⁵ In independent experiments **11** was shown to rearrange to **10** either

(9) (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

(10) K. T. Kopecky and S. Evani, *Can. J. Chem.*, **47**, 4041 (1969).

(11) F. Yoneda, K. Suzuki, and Y. Nitta, *J. Amer. Chem. Soc.*, **88**, 2328 (1966).

(12) Spectral and analytical data are in order for all new compounds. Unstable **8** was characterized only by nmr and mass spectra.

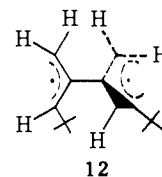
(13) Up to 5% of unidentified isomers are present. Tautomer **9** gave no hydrocarbon products on thermolysis.

(14) This compares well with the spectra for 3-methyl-2-methylene-ethylidene-cyclobutanes; J. J. Gajewski and C. N. Shih, *J. Org. Chem.*, **37**, 64 (1972).

(15) Ozonolysis produces pivaldehyde and an unstable compound thought to be 3-*tert*-butyl-1,2-cyclobutadione with ir (CCl₄) absorptions at 1735 and 1775 cm⁻¹ and λ_{\max} 510 nm. Closely analogous 3,4-di-*tert*-butyl-1,2-cyclobutadione has ir absorptions at 1758 and 1785 cm⁻¹ and λ_{\max} 536 nm [Ae. de Groot, D. Oudman, and H. Wynberg, *Tetrahedron Lett.*, 1529 (1969)].

thermally or at room temperature with iodine. These data indicate **11** to be the badly twisted syn isomer of **10**. This conclusion is also supported by nuclear Overhauser effects measured between the *tert*-butyl groups and the vinylic protons; the observed per cent enhancements in integration are shown in the structural formula (effects with ring protons were not measured).¹⁶

The original thesis of this work, that a tetramethyleneethane derivative should be formed from **8**, is substantiated. An effectively orthogonal structural arrangement **12** is virtually mandatory at some point on



the reaction profile to explain the "turning over" of the two allylic units from their initial orientation in **8** to their ultimate arrangement in **11**. It is surprising that ring closure leads nearly exclusively to sterically hindered **11** rather than **10** or another isomer. The thermal rearrangement of **11** probably also goes through a tetramethyleneethane.¹⁷ The possibility that **11** is formed from a thermally labile isomer cannot be excluded rigorously.

Related to these observations are the reports of Jacobs and coworkers¹⁸ and also Gajewski and Shih¹⁴ who find that substituents prefer syn positions on the vinylic carbons in 1,2-dimethylenecyclobutanes formed from dimerizations of allenes. The present results suggest that at least in part the preference for syn orientation lies in a remarkable facet, probably stereochemical, of the ring closure of tetramethyleneethane.¹⁹ Further work is in progress.

Acknowledgment. We thank Dr. J. de Wit of this department for carrying out the XL-100 experiments and Mr. F. A. Pinkse (University of Amsterdam) for some mass spectral measurements.

(16) Complete details of nmr experiments with **10** and **11** will be published in a full article.

(17) Similar observations have been made with the corresponding methyl-substituted compound.^{2b}

(18) (a) T. L. Jacobs, J. R. McClennon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969); (b) O. J. Muscio and T. L. Jacobs, *Tetrahedron Lett.*, 2867 (1969); (c) S. R. Byrn, E. Maverick, O. J. Muscio, Jr., K. N. Trueblood, and T. L. Jacobs, *J. Amer. Chem. Soc.*, **93**, 6680 (1971).

(19) NOTE ADDED IN PROOF. On irradiation through Pyrex at -65° in carbon disulfide, **8** is converted cleanly and exclusively to **11**.

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Carbon-Carbon Bond Formation by Selective Coupling of Alkylthioallylcopper Reagent with Allylic Halides

Sir:

The role of the allylic anion bearing a terminal arylthio group in synthetic chemistry has become increasingly apparent. Efficient and useful methods for the extension of carbon chain by means of such re-