45° during the addition. When the silane introduction was complete, an additional 150 ml. of benzene was added and the temperature was maintained at 50–55° for 2 hr. while slow introduction of hydrogen sulfide was continued. The mixture was filtered from precipitated pyridine hydrochloride in a drybox, the residue was washed once with 50 ml. of hexane (dried over Na), and the wash liquid was combined with the filtrate. Material volatile to 240° was distilled from the filtrate. The pot residue was dissolved in 150 ml. of boiling hexane plus a minimum amount (about 40 ml.) of benzene, filtered, and allowed to cool and crystallize. A total of 11.2 g. of II (m.p. 186–188°) was obtained. A second crop (3.5 g., m.p. 186–188°) was separated by partial concentration of the mother liquor. Total yield of II was 55%. II consisted of colorless, well-formed crystals of density 1.271 g./ml.; infrared bands (KBr pellet) were at 7.00, 9.01, 10.01, 13.63, 14.08, and 14.38 μ.

Anal. Calcd. for $C_{36}H_{30}S_3Si_3$; C, 67.29; H, 4.67; S, 14.96; Si, 13.08. Found: C, 67.35; H, 4.62; S, 14.40; Si, 12.90.

Failure to heat the reaction mixture after introduction of the silane resulted in reduced yields. II was only slowly hydrolyzed by atmospheric moisture, the melting point dropping only 4° after 2 days' standing in an open container in an air-conditioned laboratory.

Tetraphenylcyclodisilithiane (I).—Into a 30 × 2.5 cm. Pyrex tube connected at the top by a ground glass joint to a cold-finger trap cooled by a Dry Ice–ether slurry and then to an oil pump was placed 2.70 g. (0.004 mole) of II. The tube was suspended to a depth of 10 cm. in an electric furnace, the internal pressure was reduced to less than 1 mm., and heating was maintained at 300–315° for 2 hr. During this period, a tan crystalline solid sublimed to the cool upper walls of the tube. This solid was crystallized from 20 ml. of a hexane–benzene mixture (20% benzene by volume). Recrystallization from the same solvent gave 1.40 g. of colorless crystalline I (m.p. 163–165°; density, 1.268 g./ml.). The yield was 52% based on starting II. Remaining in the tube was 0.25 g. of a viscous glass, while 0.3 g. of an unidentified liquid was collected in the cold finger; infrared bands (KBr pellet) were at 7.00, 8.99, 10.01, 13.45, 14.04, and 14.35 μ.

Anal. Calcd. for $C_{24}H_{20}S_2Si_2$: C, 67.29; H, 4.67; S, 14.96; Si, 13.08. Found: C, 65.96; H, 4.88; S, 14.42; Si, 14.43.

A reduced yield of I (about 25%) resulted when the pyrolysis was carried out at atmospheric pressure. Admixture of I with an equal weight of II produced a material with a melting range of 149–171°.

Molecular Weight Determinations.—Molecular weights (Table I) of I and II were determined in benzene using both standard cryoscopic techniques and vapor pressure osmometric equipment.[9] In addition, the molecular weight of II was determined by the isopiestic procedure described by Childs[10] using azobenzene as the reference compound.

X-Ray Diffraction Measurements.—Table II lists principle X-ray powder photograph lines and intensities for the dimer I and the trimer II. Cu Kα radiation (Ni filter) was used. Both samples of I and II were recrystallized from a 3:1 mixture of hexane and benzene.

Acknowledgment.—The authors are indebted to Dr. Elihu Goldish for the X-ray diffraction photographs and interpretation and to Dr. John Stern, who built the vapor pressure osmometer.

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The Synthesis and Thermal Decomposition of 3,3,6,6-Tetramethyl-1,4-cyclohexadiene

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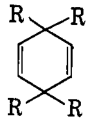
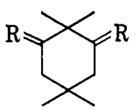
The many unusual properties[1] and reactions[2-10] of norbornadiene (I) have led us to examine other compounds having parallel nonconjugated but interacting double bonds. The simplest hydrocarbon with this structural feature is 1,4-cyclohexadiene (II), which, like I, has an ultraviolet absorption spectrum indicative of interacting π-electron systems.[1,11] Since the chemistry of II is complicated by double-bond isomerization[12] and dehydrogenation to benzene,[13] we decided to synthesize 3,3,6,6-tetramethyl-1,4-cyclohexadiene (III).

Methylation of dimedone[14] gave 2,2,5,5-tetramethylcyclohexane-1,3-dione (IV), which was reduced to a mixture of diols (V) by lithium aluminum hydride and then converted to a crystalline diacetate (VI), m.p. 64–65°,[15] by reaction with acetic anhydride. When pyrolyzed at 350°, the diacetate VI was 10% decomposed and yielded two volatile products, A and B, in a ratio of 10:1, respectively. Pure A, m.p. 7–8°, was obtained by preparative vapor phase chromatography and was identified as III by spectroscopic methods. The infrared and n.m.r. spectra and the v.p.c. retention time of product B proved to be identical with those of authentic *p*-xylene.

I



II, R = H
III, R = CH_3



IV, R = O
V, R = H, OH
VI, R = H, $OCOCH_3$

The infrared absorption spectrum of III exhibits a very strong vinyl hydrogen deformation absorption at 764 cm.$^{-1}$. The corresponding absorption for II is found at a much lower frequency (678 cm.$^{-1}$). The shift may be due to the extensive allylic substitution in III.[16]

The n.m.r. spectrum of III is particularly instructive in that two sharp resonance signals are observed at τ 4.7 and 9.0, with an area ratio of 1:3.1.

The most abundant peaks in the mass spectrum of III are listed in Table I. We tentatively assign the two intense peaks, having *m/e* of 121 and 105, to the relatively stable 1,1,4-trimethylbenzenonium ion[17] and the methyltropylium ion, respectively.

In contrast to the broad envelope of absorption bands

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[12] E. E. van Tamelen, *ibid.*, **77**, 1704 (1955).

[13] D. T. Longone and G. Smith, *Tetrahedron Letters*, **5**, 205 (1962).

[14] R. D. Desai, *J. Chem. Soc.*, 1079 (1932).

[15] This is apparently the diacetate of the *trans* diol (V) reported by A. Allen, R. Sneeden, and J. Colvin [*ibid.*, 557 (1958)].

[16] L. L. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 48.

[17] According to the nomenclature of W. von E. Doering, M. Saunders, H. Boynton, H. Earhart, E. Wadley, W. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

exhibited by I and II in the 200–250-mμ region, III shows only intense end absorption, indicating relatively little interaction of the double bonds. In I, the six-membered ring is severely folded (dihedral angle 110°)[1] as a consequence of the methylene bridge; transannular overlap of π-orbitals is thus enhanced on the *endo* side of the molecule. In II, the dihedral angle appears to be about 140°,[18,19] while in III the ring seems to be flattened even more.

TABLE I

MAJOR PEAKS[a] IN THE MASS SPECTRUM OF III

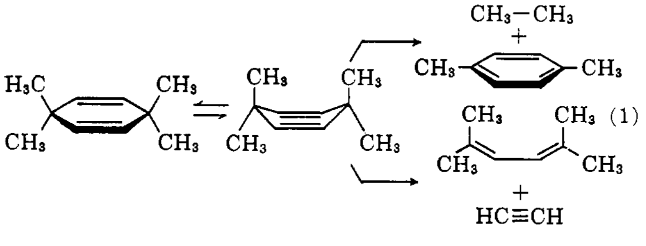
m/e	Relative abundance	*m/e*	Relative abundance
136 (P)	4.5	91	16.3
122	9.8	79	8.5
121	100.0	77	12.4
119	5.3	65	5.1
106	10.0	53	6.1
105	33.2	51	7.9

[a] Only peaks having $m/e \geq 50$ are considered.

Pyrolysis of the diacetate VI at 410° resulted in complete decomposition, with *p*-xylene as the major product (90%). That the *p*-xylene resulted from subsequent thermal decomposition of III rather than from a unique mode of acetate pyrolysis was shown by experiments in which III itself was pyrolyzed under identical conditions—*p*-xylene was the only product isolated.[20]

Gaseous products from pyrolysis of VI, trapped by liquid nitrogen, were found to contain more ethane than could be reasonably attributed to random combination of methyl radicals. For example, the liquid nitrogen condensate from pyrolysis of a benzene solution of VI at 410° was 1% methane,[21] 44% ethane, 22% ethylene, 9% propane, 18% propylene, and 6% of a C_4 mixture. Consequently we suggest that a primary mode of thermal decomposition of III is an essentially concerted expulsion of ethane.

Fragmentation of III into 2,5-dimethyl-2,5-hexadiene (VII) and acetylene is apparently negligible, since our analytical methods would have detected as little as 1–2% of VII, and authentic VII was shown to survive the pyrolysis conditions unchanged. The absence of this mode of fragmentation is quite reasonable in view of the nearly planar conformation we have assigned to the six-membered ring in III on the strength of its ultraviolet absorption. The only bonds that would overlap well with the π-orbitals during cleavage are those from the ring to the methyl groups. A referee has pointed out that thermal fragmentation of III may proceed from a vibrationally excited nonplanar conformation (eq. 1) and that the previous argument is perhaps an oversimplification. Such a conformation would also be conducive to fragmentation into VII and acetylene; however, the rate of this latter decomposition could well remain much slower than that for ethane expulsion.



(1)

Experimental

The pyrolysis apparatus employed in this work consisted of a 20-mm. Pyrex column packed with $^1/_{16}$-in. Pyrex helices to a height of 23 cm. This column was fitted with a Hershberg dropping funnel modified so that an inert gas (nitrogen or helium) sweeps through the apparatus as the reactant is slowly added. Control devices for the heating unit (±2°) and gas supply and a series of traps at the bottom of the pyrolysis column complete the system.

Analytical methods consist of gas chromatography using a 12-ft. alumina column and a 6-ft. Apiezon L (30%) column, infrared spectroscopy, mass spectroscopy, and nuclear magnetic resonance spectroscopy. Microanalysis were performed by Spang Laboratory, Ann Arbor, Michigan.

2,2,5,5-Tetramethylcyclohexane 1,3-Diacetate (VI).—Crude 2,2,5,5-tetramethylcyclohexane-1,3-diol (V, 31.7 g.), prepared by reduction of dimethyldimedon (IV)[14] with lithium aluminum hydride (2.5 moles for each mole of diketone) in tetrahydrofuran, was dissolved in 1090 ml. of dry pyridine and treated with 365 ml. of acetic anhydride. After 2 days at room temperature, the reaction mixture was quenched by adding cold methanol and yielded a viscous oil, b.p. 95–100° at 1 mm., which slowly crystallized. Further crystallizations from cold pentane and from aqueous methanol gave colorless needles, m.p. 64–65°, having a raspberry-like odor.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 65.36; H, 9.40. Found: C, 65.66; H, 9.40.

Pyrolysis of VI. A. Pyrolysis of a pentane solution of VI in a stream of helium at 350° resulted in very little decomposition. Analysis of the crude pyrolysate indicated that roughly 10% of the diacetate had reacted yielding a 10:1 mixture of 3,3,6,6-tetramethyl-1,4-cyclohexadiene (III) and *p*-xylene. These materials were isolated by preparative gas chromatography and identified spectroscopically (see text).

B.—A solution of VI (2.5 g.) in benzene (6 ml.) was slowly passed through the pyrolysis column at 410°. Helium was used as the carrier gas and the effluent was directed through three receivers cooled, respectively, by ice, Dry Ice, and liquid nitrogen. The material trapped in the first receiver was taken up in pentane, washed with dilute sodium bicarbonate, and distilled. Gas chromatographic analysis of the distilled fractions and the pot residue failed to disclose any unreacted VI and indicated *p*-xylene as the major product (50% actual yield) accompanied by traces of III.

The contents of the trap cooled by liquid nitrogen were analyzed by gas chromatography using a 12-ft. column packed with Alcoa activated alumina Grade F-1 and employing Phillips Hydrocarbon Mixture No. 40 as a standard. The results of this analysis are listed in the main part of this paper.

Pyrolysis of III.—A solution of III (200 mg.) in pentane (5 ml.) was pyrolyzed at 410°, the rate of addition and helium flow being identical with that employed in the previous experiment. The crude pyrolysate (90 mg.) proved to be an equimolar mixture of *p*-xylene and pentane.

Acknowledgment.—We are indebted to the National Science Foundation, Undergraduate Research Participation Program, for a grant to Cecelia Dzurella.

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[19] F. H. Herbstein, *J. Chem. Soc.*, 2292 (1959).

[20] After our work had been submitted for publication, H. H. Stechl [*Angew. Chem. Intern. Ed. Engl.*, **2**, 743 (1963)] reported that the photodimer of 1,3,3-trimethylcyclopropene was pyrolyzed to durene in 40% yield at 390°. The author suggested a hexamethyl-1,4-cyclohexadiene corresponding to our compound III as an intermediate.

[21] A significant amount of methane may have been lost during the vacuum-line operations that preceeded analysis.