deuterioamide **16** in 75% yield. The nmr spectrum of this compound was shown to consist of 1.72 D/molecule.

To 0.005 mol of deuterioamide **16** in 20 ml of THF at 0° was added 0.011 mol of *n*-butyllithium in hexane and the mixture was treated, after 30 min, with 0.005 mol of benzophenone in 10 ml of THF. The reaction mixture was worked up to give deuteriocarbinolamide **17** in 60% yield. This amide was shown to contain 0.98 D/molecule.

Cyclization of 17 to Form 18.—A sample of deuteriocarbinolamide **17** (1.0 g) was dissolved in 5 g of H_2SO_4 at 0° for 20 min. The reaction mixture was poured onto ice and the solution was made basic with NaOH. The crude product was collected and recrystallized from CH_3CN to give 0.56 g (58%) of **18**, mp 190–192°, containing 0.98 D/molecule (by nmr). A similar result was obtained after repeating the experiment.

Cyclodeamination of γ-Hydroxyamide 11.—As in the case of cyclodeamination of **1a**, a 1.0-g sample of **11** was refluxed with 50 ml of acetic acid overnight (*ca.* 12 hr). The product was worked up and recrystallized from aqueous DMF to give 0.62 g (65%) of 3,3,4-triphenyl-3,4-dihydroisocoumarin (**14**), mp 265–267°, ir 1720 cm^{-1} (C=O).

Anal. Calcd for $C_{27}H_{20}O_2$: C, 86.14; H, 5.35. Found: C, 85.93; H, 5.17.

Registry No.—**1a**, 2594-59-4; **1b**, 21868-83-7; **2a**, 20141-85-9; **3a**, 24097-53-8; **3b**, 24097-54-9; **13**, 24097-55-0; **14**, 24097-56-1.

Pyrolysis of Alkenylidenecyclopropane and Biscyclopropylidene Systems[1a]

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Contribution No. 1856 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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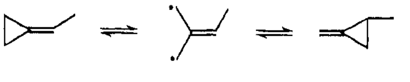
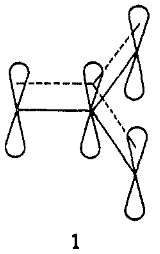
Pyrolysis of 1-(2-methylpropenylidene)-2,2,3,3-tetramethylcyclopropane (**3**) gives, in good yield, 1,2-(bisisopropylidene)-3,3-dimethylcyclopropane (**4**). The synthesis of 1,1,2,2,5,5-hexamethylbiscyclopropylidene (**15**) was accomplished by the reaction of **3** with excess methylene iodide/zinc–copper couple. Pyrolysis of **15** at 400° in a flow pyrolysis system produces 1-isopropylidene-2,2,4,4-tetramethylspiropentane (**20**) while at higher temperatures **15** leads to 2,4,5-trimethyl-3-isopropylidenehexa-1,4-diene (**21**) as well as *o*- and *p*-xylene. Pyrolysis of 1-methylene-2-isopropylidene-3,3,4,4-tetramethylcyclobutane (**29**) at 460° leads cleanly to triene **21**. At 620° **4** gives enyne **13** as well as *p*-xylene and toluene. The mechanistic details of these transformations are discussed in terms of diradical intermediates.

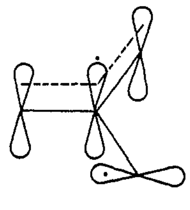
The thermal rearrangement of methylenecyclopropanes has been known for a number of years. One of the first examples was the thermolysis of Feist's ester which has been studied by Ettlinger.[2] A number of examples have since been reported which indicate that the rearrangement proceeds *via* a trimethylenemethane diradical.[3] This is illustrated below for a simple case. Gajewski[4] has recently looked at optically active methylenecyclopropanes and concluded that, in substituted



methylenecyclopropanes, the intermediate is not the planar delocalized diradical **1** but rather an orthogonal diradical represented as **2**. Consideration of these results suggests that a similar rearrangement may obtain in more complicated methylenecyclopropyl systems. This report concerns itself with alkenylidenecyclopropane and biscyclopropylidene thermal chemistry.

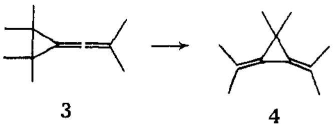


1



2

A simple entry into the alkenylidenenecyclopropane system can be effected through reaction of allenic[5] or propargylic[6] halides with *tert*-butoxide in the presence of olefins. Synthesis of **3** was achieved in good yield by reaction of 1-bromo-3-methylbuta-1,2-diene with tetramethylethylene. Pyrolysis of **3**, carried out in a flow system at 360° (0.1 mm), results in an almost quantitative conversion to dimethylenecyclopropane **4**. A similar and more instructive conversion was effected by thermolysis of alkenylidenecyclopropane **5**. Three isomeric hydrocarbons, **6**, **7**, and **8** were produced. The ratio of these products varies with temperature; the **6**:**7**:**8** ratio is 10:2:3 at 360° and 2:3:6 at 410°. Furthermore, pyrolysis of either **6** or **7** at 380° yields a mixture of the three isomeric compounds. On the other hand, **8** is recovered essentially unchanged at this temperature. Raising the temperature to 460°, however, causes partial transformation of **8** to **6** and **7**. The structural assignments of **6**, **7**, and **8** have been discussed previously.[7]



3 **4**

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[1] (a) Supported by a research grant from the National Science Foundation. (b) Public Health Service Predoctoral Fellow, 1966–1968. (c) Author to whom correspondence should be addressed. Alfred P. Sloan Research Fellow, 1968–1970. (d) Indiana University Foundation and National Science Foundation Undergraduate Research Participant, 1968–1969.

[2] M. G. Ettlinger, *J. Amer. Chem. Soc.*, **74**, 5805 (1952).

[3] J. P. Chesick, *ibid.*, **85**, 2720 (1963); E. F. Ullman, *ibid.*, **81**, 5386 (1959); **82**, 505 (1960); E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961); T. C. Shields, B. A. Shoulders, J. F. Krause, D. L. Osborn, and P. D. Gardner, *ibid.*, **87**, 3026 (1965); H. M. Frey, *Trans. Faraday Soc.*, **57**, 951 (1961).

[4] J. J. Gajewski, *J. Amer. Chem. Soc.*, **90**, 7178 (1968).

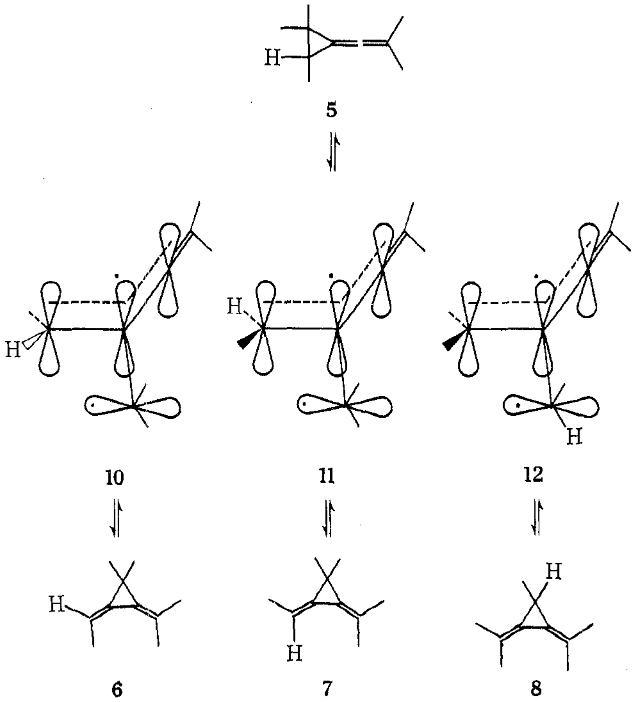
[5] S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc. C*, 1223 (1966); S. R. Landor and P. F. Whiter, *J. Chem. Soc.*, 5625 (1965).

[6] H. D. Hartzler, *J. Amer. Chem. Soc.*, **83**, 4990 (1961).

[7] J. K. Crandall and D. R. Paulson, *ibid.*, **88**, 4302 (1966).

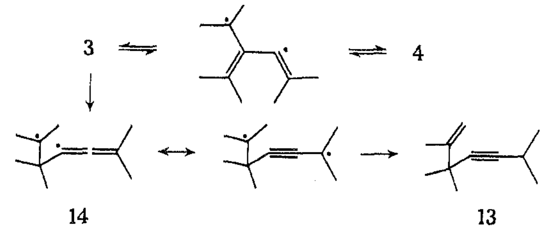
The mechanistic details of these thermal interconversions are very likely analogous to methylenecyclopropanes themselves. A similar set of orthogonal diradicals[4] can be invoked to describe this reaction. These intermediates differ from the parent system in that one of the peripheral carbon atoms is sp hybridized.[8] Scheme I depicts a rational scheme in terms of these intermediates. A number of orthogonal trimethylenemethane intermediates are possible. However, **10**, **11**, and **12** are the only ones which do not contain an unfavorable localized vinyl radical. If the rate constants for formation of products from **10**, **11**, and **12** are assumed to be nearly identical, then the kinetic preference for formation of **6** can be explained by a destabilizing half-filled *p*-orbital–methyl interaction.[4] This interaction would result in **10** being more stable than **11** or **12** and as a result the favored intermediate from **5**. At higher temperatures interconversion among the biradical intermediates and the dimethylenecyclopropanes becomes more facile and the product distribution approaches the thermodynamic equilibrium value. Each of the products can in theory be reconverted to the biradical intermediates by the reversal of its formative process and thus be repartitioned among the original three products. Compounds **6** and **7** undergo this redistribution easily but more drastic conditions are required for **8**. This is easily explained since **8** with a single stabilizing methyl on the saturated center requires a greater activation energy for bond homolysis than either **6** or **7** which give tertiary radicals at this sight.

SCHEME I

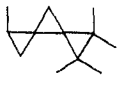


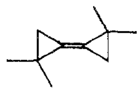
Pyrolysis of dimethylenecyclopropane **4** (or its precursor **3**) at 520° gives a mixture of **4** (39%) and enyne **13** (48%). The structure of **13** was clearly defined by its spectroscopic properties: the infrared spectrum of **13** shows a terminal double bond (6.08 and 11.1 μ), while the ultraviolet spectrum is characteristic of a nonconjugated acetylene.[9] This transformation is visualized in Scheme II. The formation of enyne **13** appears to require funneling through a small equilibrium concentration of **3** to diradical **14**. A 1,6 hydrogen transfer mechanism then leads directly to **13**.[10]

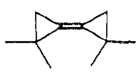
SCHEME II



A second type of methylenecyclopropane, in which the double bond is exocyclic to two cyclopropyl rings (*i.e.*, a biscyclopropylidene) can be envisioned to undergo a simple methylenecyclopropane rearrangement to produce a methylenespiropentane. This type of rearrangement has been realized in the case of **15**. A surprisingly simple and convenient synthesis of **15** was effected by treatment of alkenylidenecyclopropane **3** with a large excess of the Simmons–Smith reagent.[11] This reaction produced predominantly biscyclopropylidene **15** in good yield. Under different experimental conditions it was possible to isolate the other monoadduct **16** and the diadduct **17**. An alternate synthesis was realized using the diethyl zinc–methylene iodide[12] modification of the Simmons–Smith to give **15** exclusively in 40% yield. Biscyclopropylidene **15** displays spectral data consistent with the assigned structure and similar to model compounds **18** and **19**.[13] Predominate formation of **15** over **16** can be predicted on the basis of both steric and electronic factors.[14]


17


18


19

Pyrolysis of **15** in a flow system at 400° (0.1 mm) proceeds smoothly to give starting material (4%), methylenespiropentane **20** (87%), and its structural isomer **16** (9%). The ir spectrum of **20** shows a weak methylenecyclopropane band[15] at 5.55 μ and its nmr displays a two-proton AB quartet[16] centered at τ 9.38 ($\Delta v = 10.3$ Hz, $J = 4.0$ Hz), four methyls on saturated carbon and two olefinic methyls. An independent

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(8) This argument makes the reasonable assumption that the destablizing interaction of a methyl group and a p orbital would be greater for a half-filled p orbital than for a p orbital involved in double bond formation.

(9) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, pp 54–55.

(10) Although not usually a favored process, a similar 1,6 hydrogen shift has apparently been detected: R. F. Bleiholder, *Diss. Abstr. B*, **27**, 1080 (1966).

(11) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

(12) J. Furulsowa, N. Kawabata, and J. Nishimura, *Tetrahedron Lett.*, 3353 (1966); *Tetrahedron*, **24**, 53 (1968).

(13) B. du Laurens, A. Bezaguet, G. Davidovics, M. Bertrand, and J. Chouteau, *Bull. Chim. Soc. Fr.*, 799 (1967).

(14) J. K. Crandall, D. R. Paulson, and C. A. Bunnell, *Tetrahedron Lett.*, 5063 (1968).

(15) W. Rahman and H. G. Kuivilla, *J. Org. Chem.*, **31**, 722 (1966).

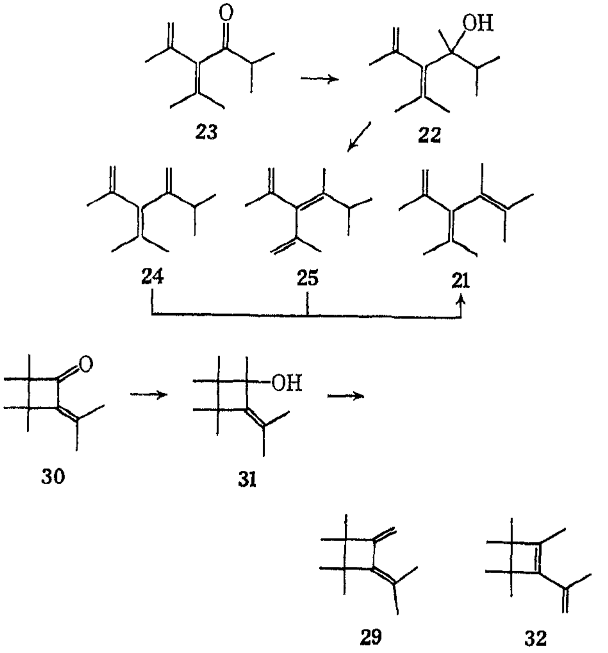
(16) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 102.

synthesis of **20** was realized by treatment of dimethylenecyclopropane **4** with Simmons-Smith reagent.[11]

Thermolysis of methylenespiropentane **20** under the above conditions did not result in reversal to **15**, but at higher temperature (510°) this material was connected to a mixture of 37% **20**, 31% triene **21**, and quite unexpectedly *p*-xylene (13%) and *o*-xylene (5%). Even more surprising was the extent of xylene formation at higher temperatures; for instance, at 610° the *p*- and *o*-xylene were isolated in 50 and 33%, respectively. Pyrolysis of isomer **16** gave similar results. At 520° triene **21** and *p*-xylene were obtained in the ratio of 7:1 while at 610° a mixture of triene **21**, *p*-xylene, and *o*-xylene were formed in the ratio of 1:21:14.

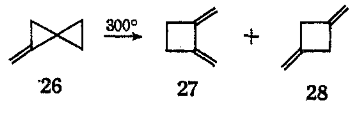
The structure of triene **21** was readily verified by its straightforward synthesis as shown in Scheme III.

SCHEME III



Alcohol **22** was obtained in 87% by methyllithium addition to ketone **23**.[17] Dehydration of **22** in sulfuric acid-acetic acid gave a mixture of 25% **24**, 51% **25**, and 24% of the desired triene **21**. Pyrolysis of this mixture of triene at 490° cleanly transformed **24** and **25** into the more stable isomer **21**. These transformations are readily interpreted in terms of 1,5 hydrogen shifts.

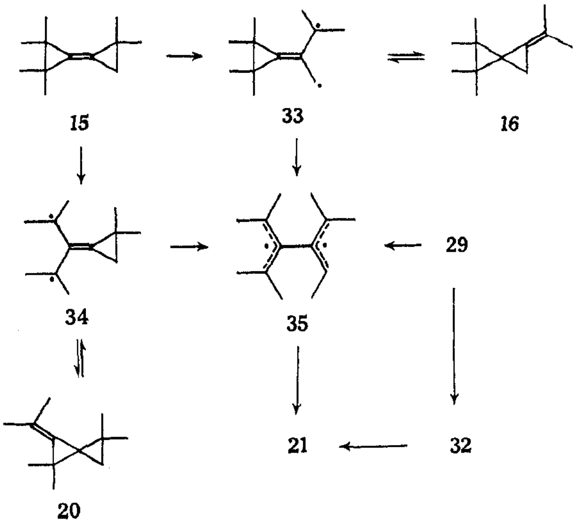
While this work was in progress, Dolbier reported on the thermolysis of the parent methylenespiropentane **26**.[18] At temperatures above 300° compound **26** isomerizes to a 7:1 mixture of **27** and **28**. This observation prompted an investigation of the thermolysis of the analogous 1,2-dimethylenecyclobutane **29** which would be expected in the present system. Its synthesis is also outlined in Scheme III. Treatment of ketone **30**[17] with methyllithium gave alcohol **31** in almost quantitative yield. Dehydration of **31** in phosphorus oxychloride-pyridine produced a mixture of **29** (52%) and **32** (48%). A convenient isolation of **29** from this mixture was effected by pyrolysis of the reaction product at 360° which gives 52% **21**, 2% **32**, and 46% unchanged **29**. This procedure proved convenient since a mixture of triene **21** and diene **29** can easily be separated by preparative glpc while the same is not true of the original mixture. The pyrolytic conversion of **32** to **21** is readily interpreted as a simple cyclobutene to butadiene thermal isomerization. Kiefer and Tanna[19] have recently studied several very similar pyrolytic conversions.



Pyrolysis of diene **29** at 460° afforded 72% triene **21**, 4% starting material, and a number of minor products. This experiment clearly demonstrates why diene **29** is absent from the thermolysis products of **15**, **16**, or **20**, since this material would not have accumulated in the 460° pyrolysate even if it were an important product. At 460° very little, if any, isomerization of **20** occurs.

A reasonable mechanism for the thermal rearrangements of **15**, **16**, and **20** is shown in Scheme IV. Doering and Gilbert[20] have summarized strong evidence that the thermal rearrangement of spiropentane systems involve diradical intermediates rather than concerted processes. The rearrangements undergone by **15**, **16**, and **20** are also best described in terms of such diradical intermediates. The biscyclopropylidene **15** is converted to isomers **16** and **20** *via* the respective trimethylenemethane intermediates **33** and **34**. Pyrolysis of **16** or **20** does not result in any back reaction to form **15** in agreement with the predicted lower thermal stability of **15**. The preference for products derived from **34** rather than **33** is a reflection of the stabilization of alkyl groups on the radical centers and relief of nonbonded interaction in the transition state leading to **34**. There is no evidence for appreciable interconversion of **15** and **16** in support of this kinetic argument. At more elevated temperatures the cyclopropyl ring in the reversibly formed intermediates **33** and **34** is cleaved leading to the interesting bisallyl diradical **35**. This process is postulated to involve collapse of the cyclopropyl radical moiety of the trimethylenemethane in-

SCHEME IV



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[17] J. K. Crandall and D. R. Paulson, *J. Org. Chem.*, **33**, 991 (1968).

[18] W. R. Dolbier, Jr., *Tetrahedron Lett.*, 393 (1968).

[19] E. F. Kiefer and C. H. Tanna, *J. Amer. Chem. Soc.*, **91**, 4478 (1969).

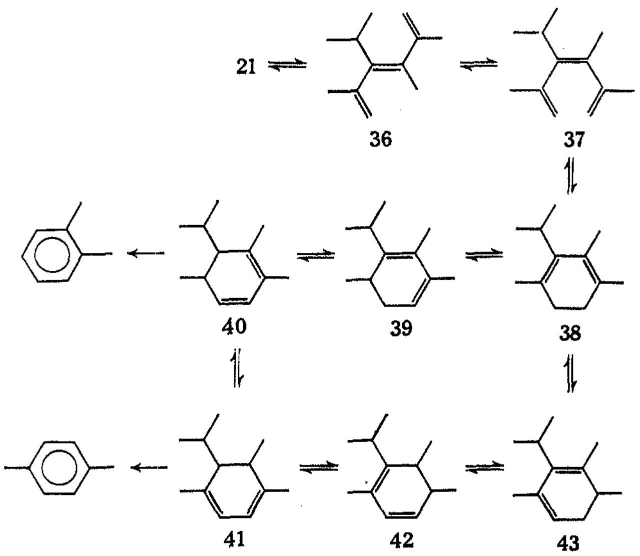
[20] W. E. Doering and J. C. Gilbert, *Tetrahedron, Suppl.*, **7**, 397 (1966).

termediates **33** and **34**. Cyclopropyl radicals are known to rearrange thermally to allylic radicals with an activation energy of less than 18 kcal/mol,[21] although they appear to maintain their structural integrity at lower temperatures.[22] The presence of an appreciable energy barrier for the cyclopropyl radical to allyl radical interconversion is also apparent in the present rearrangement. Other modes of bond breakage in **15**, **16**, or **20** would lead to intermediates of much higher energy and, in addition, not provide a straightforward pathway to triene **21**. Diradical **35** leads readily to triene **21** by disproportionation through a favorable six-center hydrogen transfer. Gajewski[23] has recently observed similar 1,5 hydrogen transfers *via* bisallyl biradicals.

At least two paths can be recognized for the conversion of dimethylenecyclobutane **29** into triene **21**. The first of these is initiated by homolytic cleavage of **29** to bisallyl diradical **35**, an intermediate in the main sequence described above. The second pathway proceeds *via* a concerted 1,5 hydrogen shift to yield cyclobutene **32** followed by the experimentally demonstrated isomerization of **32** to **21**.

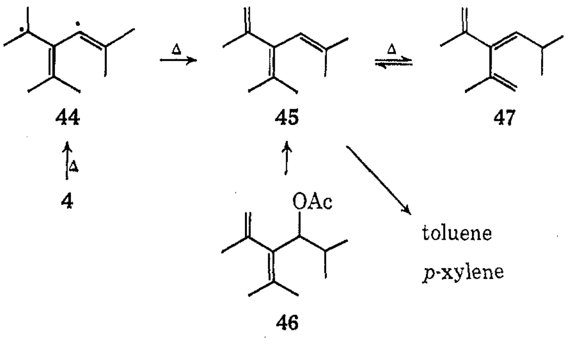
One of the most interesting problems connected with this study involves the mode of formation of *o*- and *p*-xylene. Since pyrolysis of triene **21** at 580° gives 50% *p*-xylene and 30% *o*-xylene, it is likely that **21** is an intermediate in the formation of the xylenes from **15**, **16**, and **20**. A plausible mechanism for these novel transformations is shown in Scheme V. Concerted 1,5 hydrogen shifts interconvert the trienes **21** and **36**. This general type of rearrangement has been carefully studied by several groups.[24] The well-precedented cyclization pictured for triene **37** can take place only from the cis olefin.[25] Presumably trans olefin **36** provides this configuration by thermal isomerization. The cyclohexadienes **38** through **43** are also proposed to equilibrate by 1,5 hydrogen shifts. Similar hydrogen transfers have been observed before in cyclohexadienes.[25] Loss of the elements of butane from the key intermediates **40** and **41** would lead to *o*-xylene and *p*-xylene directly. There are several reports concerning the loss of the elements of hydrogen or low-molecular-weight hydrocarbons to form aromatic products during the pyrolysis of cyclohexadienes.[26] It was originally suspected that an intact molecule of isobutane might be formed in this elimination. However, the major gaseous hydrocarbons from the pyrolysis of triene **21** at 620° were propylene and ethylene. The exact process by which the elements of butane are lost appears to be a rather complex one, and is probably free radical in nature.

SCHEME V



A similar series of transformations occurs when dimethylenecyclopropane **4** is pyrolyzed at high temperature. At 620° compound **4** gives 50% enyne **13**, 30% *p*-xylene, 8% toluene along with at least six unidentified minor products. It was independently shown that enyne **13** is not an intermediate in the formation of the aromatic compounds. A mechanism analogous to that shown in Scheme V is proposed. Trimethylenemethane diradical **44** undergoes 1,4 hydrogen abstraction[27] to form triene **45** which yields the aromatic hydrocarbons by a process similar to that elaborated in Scheme V for triene **21**. Pyrolysis transformation of an authentic sample of triene **45** to the observed aromatics demonstrates the viability of this proposal.

Triene **45** was prepared by hydride reduction of ketone **23** followed by acylation to give acetate **46**. Pyrolysis of **46** in a flow system at 420° gave a 1:1 mixture of trienes **45** and **47**; at 460° the ratio was 3:1. The presence of both **45** and **47** in the pyrolysis of acetate **46** is accounted for by equilibration of acetate **46** and its allylic isomer prior to elimination of acetic acid[28] and/or by thermal interconversion of **45** and **47** by 1,5 hydrogen migration.



Experimental Section

General.—Infrared spectra (ir) were obtained with Perkin-Elmer Model 137 and 137G infrared spectrophotometers in carbon tetrachloride solution unless otherwise specified. Nuclear magnetic resonance (nmr) spectra were obtained with Varian

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[21] A. S. Gordon, *Pure Appl. Chem.*, **5**, 441 (1962).

[22] D. I. Schuster and J. D. Roberts, *J. Org. Chem.*, **27**, 51 (1963).

[23] J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **91**, 5900 (1969).

[24] J. Wolinski, B. Chollar, and M. D. Baird, *ibid.*, *Soc.*, **84**, 2775 (1962); H. M. Frey and R. J. Ellis, *J. Chem. Soc.*, 4770 (1965).

[25] E. N. Morrell, G. Caple, and B. Schatz, *Tetrahedron Lett.*, 385 (1965).

[26] H. Pines and R. H. Kozlowski, *J. Amer. Chem. Soc.*, **78**, 3776 (1956); H. Pines and C. T. Chen, *ibid.*, **81**, 928 (1959); G. Dupont and R. Dulou, *Bull. Chim. Soc. Fr.*, C-29 (1951).

[27] At least one example of a 1,4 hydrogen migration to a vinyl radical has been documented: J. A. G. Dominguez and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 940 (1962); S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, **16**, 397 (1965).

[28] W. J. Bailey and R. Barclay, Jr., *J. Org. Chem.*, **21**, 328 (1956).

A-60 and HR-100 spectrometers in carbon tetrachloride solution. Ultraviolet spectra (uv) were recorded on a Cary 14 spectrophotometer. Raman spectra were taken on a Cary 81 spectrophotometer. Mass spectra were obtained with an AEI MS-9 mass spectrometer at 70 eV. Gas chromatography (glpc) was performed on Aerograph Model 600 and Model 1200 chromatographs. The analytical column was 10 ft × $^1/_8$ in. 15% Carbowax 20M on 60–80 Chromosorb W; preparative columns were 10 ft × $^3/_8$ in. or 20 ft × $^3/_8$ in. 30% Carbowax 20 Mon 60–80 Chromosorb W or 10 ft × $^3/_8$ in. 30% Ucon polar 2000 on 60–80 Chromosorb W. Percentage composition data were estimated by peak areas.

1-(2-Methylpropenylidene)-2,2,3,3-tetramethylcyclopropane (3). **A.**—A mixture of 30 g of tetramethylethylene and 10 g of potassium *tert*-butoxide was stirred under a nitrogen atmosphere for 10 min, after which 11.7 g of freshly distilled 1-bromo-3-methyl-1,2-butadiene was added over a 30-min period. The mixture was stirred at room temperature for 3 hr and 100 ml of pentane was added. The reaction mixture was suction filtered through a sintered-glass Büchner funnel containing Hyflow-Supercel filter aid. The pentane was distilled from the reaction mixture and the residue was eluted with hexane through a short column of Florisil. Removal of the hexane by flash evaporation gave 7.0 g (60%) of **3**. A recrystallized sample has mp 48–48.5°, (lit.[6] mp 48.6–49.3°).

B.—Using the procedure of Hartzler,[6] yields of **3** on the order of 25–30% were obtained.

1,2-Bis(isopropylidene)-3,3-dimethylcyclopropane (4).—A 137-mg sample of **3** was pyrolyzed at 360° and 0.25 mm. The pyrolysis was carried out on a vacuum pyrolysis system consisting of a glass-helices packed Pyrex column, 10 mm × 130 mm, passing through an E. H. Sargent and Co. tube furnace. The sample was placed in a 5-ml flask attached at one end of the tube and a Dry Ice trap, 20 mm × 150 mm, was attached to the other end of the tube. Vacuum was applied at the trap and the pyrolysis product collected in the trap. The pyrolysis gave 131 mg (96%) of 1,2-bis(isopropylidene)-3,3-dimethylcyclopropane (**4**). The spectral properties of this product agree in detail with those reported by Schecter.[29]

1-(2-Methylpropenylidene)-2,2,3-trimethylcyclopropane (5).—Using the procedure of Hartzler,[6] 23.2 g of potassium *tert*-butoxide, 60 g of 2-methyl-2-butene and 18.5 g of 3-chloro-3-methylbutyne gave 5.5 g (24%) of **5**.

Pyrolysis of 5.—A 1.0-g sample of **5** was pyrolyzed on the vacuum pyrolysis system at 360° to give 0.90 g of crude product. Glpc analysis showed 26% **5** and three products as 11, 48, and 15% of the reaction product. The 11% product was identified as *anti*-1-ethylidene-2-isopropylidene-3,3-dimethylcyclopropane (**7**): ir 5.56 and 6.03 μ; nmr τ 8.76 (s, 6), 8.2 (m, 9), and 4.42 (quartet, 1, J = 7.0 Hz); uv max (hexane) 244 mμ (ε 18,700) and 254 mμ (15,700); mass spectrum with a strong molecular ion at m/e 136.

The 48% product was shown to be *syn*-1-ethylidene-2-isopropylidene-3,3-dimethylcyclopropane (**6**): ir 5.56 and 6.06 μ; nmr τ 8.84 (s, 6), singlets at 8.19 and 8.09 overlapping a doublet in the same region (9 protons total), 4.60 (quartet, 1, J = 7.0 Hz); uv max (hexane) 245 mμ (ε 20,000) and 253 (17,500); mass spectrum with a strong molecular ion at m/e 136.

The 15% product was identified as 1,2-bisisopropylidene-3-methylcyclopropane (**8**): ir 5.53 and 6.05 μ; nmr τ 8.89 (distorted doublet, 3, J = ∼6 Hz) and 8.1 (m, 13); uv max (hexane) 251 mμ (ε 19,700) and 262 (18,560); mass spectrum with a strong molecular ion at m/e 136.123 (Calcd for $C_{10}H_{16}$: 136.125).

Pyrolysis of a 1.0-g sample of **33** at 410° on the vacuum pyrolysis system gave 0.95 g of crude product. Glpc analysis showed **7**, **6**, and **8** in the ratio of 2:3:6.

Pyrolysis of 7, 6, and 8.—A 5 mg sample of **7** was pyrolyzed on the vacuum pyrolysis system at 380°. Glpc analysis of the crude product showed **7**, **6**, and **8** in the ratio of 5:2:1. Using the same procedure on 5 mg of **6** gave **7**, **6**, and **8** in the ratio of 2:2:1. Compound **8** remained essentially unchanged by these conditions. However at 460° **8** gives **7**, **6**, and **8** in the ratio of 3:2:5.

High Temperature Pyrolysis of 3 and 4.—The following products (Table I) were obtained from pyrolysis of **3** and **4** on the vacuum pyrolysis system at 0.25 mm. The products were purified by preparative glpc.

TABLE I

Reactant (mg)	Temp, °C	**4**, %	**13**, %	*a*	*b*	*c*	Yield, mg
3 (320)	500	63	33			1	290
3 (440)	560	39	48			4	310
3 (490)	600	3	51	17	5	5	390
3 (312)	620		50	30	8	6	280
4 (70)	520	48	47			3	62

[a] % of *p*-xylene. [b] % of toluene. [c] Number of other products.

Pyrolysis of 13 at 620°.—A 40-mg sample of **13** was pyrolyzed on the vacuum pyrolysis system at 620° and 0.20 mm. Glpc and nmr analysis of the crude product showed **13** as 50% of the sample along with a large number of products. None of these minor products account for more than 5% of the mixture.

Pyrolysis of 45.—A 5-mg sample of **45** was pyrolyzed on the vacuum pyrolysis system at 620° and 0.20 mm. Glpc analysis of the crude product showed 66% *p*-xylene and 12% toluene. A 0.12-g sample of 65% **47** and 35% **45** was pyrolyzed under the same condition to give 0.08 g of crude product. Glpc analysis showed 65% *p*-xylene and 15% toluene. No other product accounted for more than about 2% of the crude product. The presence of *p*-xyelne and toluene was clearly demonstrated by nmr and ir spectral data.

2,5-Dimethyl-3-isopropylidene-4-acetoxyhex-1-ene (46).—A solution of 25 ml of pyridine, 1.35 g of acetic anhydride, and 0.92 g of 2,5-dimethyl-4-isopropylidenehex-5-en-3-ol was heated at 85° for 12 hr and cooled to room temperature, and three drops of water were added. The resulting mixture was stirred for 15 min, poured into 100 ml of water, and extracted with four 50-ml portions of pentane. The combined pentane extracts were washed with 5% hydrochloric acid solution and dried. Removal of the solvent gave 0.98 g of crude product. Glpc analysis showed the sample to be 87% **46**: ir 5.78 (OAc), 6.14 ($C{=}C$), 8.91, 9.8, and 11.1 μ ($C{=}CH_2$, strong); 100 MHz nmr τ 9.10 (d, 3, J = 8.0 Hz), 9.16 (d, 3, J = 8.0 Hz), 8.31 (s, 3), 8.21 (s, 3), 8.19 (s, 3), 8.02 (s, 3), 5.45 (m, 1), 4.97 (m, 1), and 4.66 (d, 1, J = 10.0 Hz).

Pyrolysis of 46.—A 218-mg sample of **46** was pyrolyzed on the vacuum pyrolysis system at 420° and 0.25 mm. The crude product was dissolved in 25 ml of pentane, washed with 10 ml of saturated sodium bicarbonate solution, and dried. Removal of the pentane by flash evaporation gave 162 mg of crude product. Glpc analysis showed two major products as 50 and 47% of the volatile reaction product. Preparative glpc collection showed the 50% product to be 2,5-dimethyl-3-isopropenylhexa-1,3-diene (**47**): ir 6.1 ($C{=}C$), 6.2 ($C{=}C$), 7.3, 10.4, and 11.2 μ ($C{=}CH_2$, strong); 100 MHz nmr τ 9.04 (d, 6, J = 7.0 Hz), 8.19 (m, 3), 8.13 (m, 3), 7.4 (m, 1), 5.34 (m, 1), 5.12 (m, 1), 5.07 (m, 1), and 4.82 (m, 1); uv max (hexane) 233 mμ (ε 20,000); mass spectrum with a molecular ion at m/e 150.1410 (Calcd for $C_{11}H_{18}$: 150.1408).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.52; H, 11.85.

The 47% product was shown to be 2,5-dimethyl-3-isopropylidenehexa-1,4-diene (**45**): ir 6.2 ($C{=}C$), 7.3, and 11.2 μ ($C{=}CH_2$); 100 MHz nmr τ 8.45 (s, 3), 8.41 (s, 3), 8.25 (m, 9), 5.40 (m, 1), 5.13 (m, 1), and 4.45 (m, 1), uv max (hexane) 220 mμ (ε 9600).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.92; H, 12.00.

1,1,2,2,5,5-Hexamethylbiscyclopropylidene (15).—To predried flask was added 100 ml of anhydrous ether, 72.3 g of methylene iodide, 17.55 g of zinc–copper couple, and a crystal of iodine. The ethereal solution was heated to reflux until the iodine color disappeared and 2.76 g of 1-(2-methylpropenylidene)-2,2,3,3-tetramethylcyclopropane (**3**) in 50 ml of ether was added dropwise. After 12 hr of reflux, the mixture was filtered and washed with two 50-ml portions of saturated ammonium chloride solution, three 50-ml portions of saturated sodium bicarbonate solution, and three 50-ml portions of saturated sodium chloride solution. The ether was removed by flash evaporation and the product (insoluble in methylene iodide) was purified by trap to trap distillation at 25° and 0.3 mm to give 2.2 g (75%) of 1,1,2,2,5,5-hexamethylbiscyclopropylidene (**15**): ir 7.3, 8.9, 9.4, and 10.5 μ; 100 MHz nmr τ 9.08 (s, 2), 8.87 (s, 6), 8.86 (s, 6), and 8.84 (s, 6).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.60; H, 12.19.

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[29] R. F. Bleiholder and H. Shechter, *J. Amer. Chem. Soc.*, **86**, 5032 (1964).

Under conditions of longer reaction time, more concentrated solutions and larger excesses of the Simmons-Smith reagent, crude yields ranging from 70–90% were obtained. Glpc analysis showed three major products formed in nonreproducible ratios ranging 6–12:2–24:1. The products were separated by column chromatography from a silver nitrate–silica gel column prepared from 160 g of silica gel and 21 g of silver nitrate. The products were further purified by preparative glpc.

The first product was identified as **15**. The second product was identified as 1,1,2,2,5,5-hexamethyldispiro[2.0.2.1]heptane (**17**): ir (neat) 7.3, 8.9, 9.0, and 9.1 μ; 60 MHz nmr τ 9.50 (m, 2), 9.32 (m, 2), 9.01 (s, 3), 8.96 (s, 6), 8.93 (s, 6), and 8.86 (s, 3).

Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.54; H, 12.41.

The third product was identified as 1-isopropylidene-4,4,5,5-tetramethylspiro[2.2]pentane (**16**): ir 7.3, 8.2, 9.0, 9.2, 9.7, 10.4, and 11.0 μ; 60 MHz nmr τ 9.15 (m, 2), 8.91 (s, 6), 8.85 (s, 6), and 8.21 (m, 6). Mass spectral analysis of the molecular ion gave *m/e* 164.1572 (Calcd for $C_{12}H_{20}$: 164.1565).

Reaction of Diethylzinc with 3.—To a predried flask was added 8 g (54 mmol) of **3** and 150 ml of anhydrous ether. The ethereal solution and a sample of diethylzinc, prepared by Noller's method,[30] were degassed, and 12.5 ml (120 mmol) of diethylzinc was vacuum transferred to the reaction flask at 0.01 mm and −180°. The system was flushed with nitrogen and the reaction flask was transferred to an oil bath. Care was taken to keep oxygen and water from the reaction mixture. As a solution of 2.8 g ether was added dropwise, the reaction mixture was refluxed under a nitrogen atmosphere. The solution was refluxed for 18 hr, cooled, and 100 ml of saturated ammonium chloride was very cautiously added. The ether layer was separated, washed with a 100-ml portion of saturated sodium bicarbonate solution, two 100-ml portions of saturated sodium chloride solution, and dried. The solvent was removed by flash evaporation and the residue vacuum distilled at 0.25 mm and 25°. A crude yield of 4.42 g was obtained. Glpc analysis showed **15** to be the exclusive product. Spectral data confirmed the results.

Pyrolysis of 15.—A 335-mg sample of **15** was pyrolyzed in the flow system at 0.25 mm and 400°. Glpc analysis showd **15** (4%), **20** (87%), and **16** (9%). Compounds **20** and **16** were purified by preparative glpc and identified by spectral data.

Pyrolysis of 16.—A 10-μl sample of **16** was pyrolyzed in the flow system at 520° and 0.25 mm. Glpc retention time comparison on a 250 ft × $^1/_{100}$ in. UCON polar capillary column showed that **21** and *p*-xylene were obtained in the ratio 6.5:1.

A 10-μl sample of **16** was pyrolysed in the flow system through a quartz-chip packed quartz tube at 610° and 0.25 mm. Glpc retention time comparison on the capillary column showed **21** and *p*- and *o*-xylene in the ratio 1:21:14.

1-Isopropylidene-2,2,4,4-tetramethylspiro[2.2]pentane (20).—To a predried flask was added 150 ml of ether, 27.0 g of methylene iodide, 6.6 g of zinc–copper couple, and a crystal of iodine. The resulting mixture was stirred under reflux until the iodine color disappeared and 0.5 g of 1,2-bisisopropylidene-3,3-dimethylcyclopropane (**4**) in 25 ml of ether was added dropwise. After 5 days of reflux the reaction mixture was cooled and filtered, and the solid residue washed well with ether. The combined ethereal portions were washed with two 100-ml portions of saturated ammonium chloride solution, two 100-ml portions of saturated sodium bicarbonate solution, 100 ml of saturated sodium chloride solution, and dried. The ether was removed by distillation through a 6-in. glass helices packed column to give 0.52 g of crude product. Glpc analysis of the crude product showed 50% of **4** and 50% of 1-isopropylidene-2,2,4,4-tetramethylspiro[2.2]-pentane (**20**): ir 5.55 (very weak), 7.15, 7.35, 9.0, 9.2, 9.5, 9.9, and 10.5 μ; 100 MHz nmr AB pattern centered at τ 9.38 (2, $\Delta\nu$ = 10.3 Hz, J = 4.0 Hz), 9.01 (s, 3), 8.95 (s, 3), 8.93 (s, 3), 8.91 (s, 3), 8.44 (s, 3), and 8.34 (s, 3).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.55; H, 12.34.

2,3,5-Trimethyl-4-isopropylidenehex-5-en-3-ol (22).—To a predried flask containing a solution of methyl lithium (prepared from 0.14 g of lithium wire and 1.42 g of methyl iodide in 20 ml of ether) under a nitrogen atmosphere was added dropwise a solution of 0.40 g of 2,5-dimethyl-4-isopropylidenehex-5-en-3-one (**23**) in 20 ml of ether. After stirring at room temperature for 2 hr, 10 ml of water was added dropwise with cooling, the resulting mixture was poured into 50 ml of water and extracted with three 50-ml portions of ether. The combined ethereal fractions were dried and the ether removed on the flash evaporator to give 0.40 g of crude product. Glpc analysis showed the sample to be 87% **22** and 13% **23**. Glpc collection gave pure **22**: ir 2.77 (OH), 3.23 (=CH), 6.0 (C=C), 6.1 (C=C), 10.8, and 11.5 μ ($C=CH_2$); 100 MHz nmr τ 9.10 (m, 6), 8.68 (d, 3), 8.34 (m, 3), 8.22 (s, 3), 8.16 (m, 3), 7.82 (m, 1), 5.42 (m, 1), and 5.00 (m, 1).

Dehydration of 22.—A 0.22-g sample of **22** was dissolved in 25 ml of glacial acetic acid containing 8 drops of concentrated sulfuric acid. After stirring for 30 min, the reaction was poured into 100 ml of water and extracted with five 50-ml portions of pentane. The combined pentane extracts were washed with 50 ml of saturated sodium bicarbonate solution and dried, and the pentane removed by flash evaporation to give 0.19 g of crude product. Glpc analysis showed three major products as 25, 51 and 24% of the reaction product.

The 25% product was identified as 2,5-dimethyl-3-isopropylidene-4-methylenehex-1-ene (**24**): ir 3.2 (=CH), 6.15 (C=C), 7.35, 9.2, and 11.15 μ ($C=CH_2$, strong); 100 MHz nmr τ 9.04 (d, 6, J = 7.0 Hz), 8.43 (s, 3), 8.26 (s, broad, 6), 7.10 (septet, 1, J = 7.0 Hz), 5.35 (m, 2), and 5.07 (m, 2).

The 51% product was shown to be 2,4,5-trimethyl-3-isopropenylidenehexa-1,3-diene (**25**): ir 3.2 (=CH), 6.12 (C=C), 7.3, and 11.12 μ ($C=CH_2$, strong); 100 MHz nmr τ 9.03 (d, 6, J = 6.5 Hz), 8.32 (s, 6), 8.26 (s, 3), 7.65 (septet, 1, J = 6.5 Hz), 5.36 (m, 2), and 5.06 (m, 2); uv max (hexane) 225 mμ (ϵ 10,000); mass spectrum with a molecular ion at *m/e* 164.1575 (Calcd for $C_{12}H_{20}$: 164.1565).

The 24% product was identified as 2,4,5-trimethyl-3-isopropylidenehexa-1,4-diene (**21**): ir 3.20 (=CH), 6.12 (C=C), 7.3, 9.2, and 11.2 μ ($C=CH_2$, strong); 100 MHz nmr τ 8.51 (s, 3), 8.44 (s, 3), 8.36 (m, 9), 8.31 (s, 3), 5.37(m, 1), and 5.07 (m, 1); uv max (hexane) 216 mμ (ϵ 12,500).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.47; H, 12.19.

Pyrolysis of 15 and 20.—The following pyrolysis products were obtained upon pyrolysis of **15** and **20** in a vacuum pyrolysis system at 0.25 mm. On each run there were a number of relatively minor products present. The major products were obtained by washing the pyrolysis system trap with ether and collecting each product by preparative glpc. These products were then compared directly with authentic samples. The pecentages listed are percentages of total volatile material (Table II).

TABLE II

Reactant (mg)	Temp, °C	**20**, %	**21**, %	A, %[a]	B, %[b]	Crude yield, mg
15 (108)	500	47.0	22.6	12.5	2.4	78
15 (60)	520	7.7	51.5	12.9	2.9	46
15 (48)	540		36.1	27.6	15.1	32
15 (114)	560		20.7	33.0	21.8	98
20 (24)	510	36.7	30.5	13	4.4	18
20 (19)	600			50	32.7	15

[a] A, % *p*-xylene. [b] B, % *o*-xylene.

1,3,3,4,4-Pentamethyl-2-isopropylidenecyclobutan-1-ol (31).—To a predried flask containing a solution of methyllithium (prepared from 0.50 g of lithium wire, 50 ml of anhydrous ether, and 5.1 g of methyl iodide) under a nitrogen atmosphere was added dropwise a solution of 3.0 g of 2-isopropylidene-3,3,4,4-tetramethylcyclobutanone (**30**) in 25 ml of ether. After stirring at room temperature for 45 min, 25 ml of water was added dropwise with cooling. The resulting mixture was poured into 100 ml of water and extracted with four 100-ml portions of ether. The combined ethereal portions were dried and the solvent removed by flash evaporation to give 3.15 g of crude product. Glpc analysis showed 97% of **31** and 3% of **30**. Glpc collection gave **31**: mp 64.5–65.5°; ir 2.72 (OH), 2.84 (OH), 5.88, 7.3, 7.6, 9.1, 9.2, 9.4, 10.5, and 11.4 μ; 100 MHz nmr τ 9.09 (s, 3), 9.03 (s, 3), 8.89 (s, 6), 8.68 (s, 3), 8.40 (s, 3), 8.26 (s, 3), and 8.10 (s, 1, OH).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.07; H, 11.99.

Dehydration of 31. A.—To a solution of 0.31 g of **31** in 20 ml of glacial acetic acid was added 10 drops of concentrated sulfuric acid. After stirring for 1 hr, the resulting solution was poured

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[30] C. R. Noller, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 184.

into 50 ml of water and extracted with four 50-ml portions of pentane. The combined pentane extracts were dried and the pentane removed by flask evaporation to give 0.23 g of crude product. Glpc analysis showed 42% **21**, 8% of an unidentified compound and 35% of 1-methylene-2-isopropylidene-3,3,4,4-tetramethylcyclobutane (**29**): ir 3.21 (C=CH), 6.0 (C=C), 6.12 (C=C), and 11.6 μ (C=CH$_2$, strong); 100 MHz nmr τ 8.98 (s, 6), 8.87 (s, 6), 8.29 (s, 3), 8.25 (s, 3), 5.36 (m, 1), and 5.19 (m, 1); uv max (hexane) 248 mμ (ε 14,300).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.40; H, 12.11.

B.—To a solution of 3.5 g of **31** in 30 ml of pyridine was added dropwise a solution of 4.0 g of phosphorous oxychloride in 20 ml of pyridine. After stirring for 4 hr, the reaction mixture was poured into 100 ml of water and extracted with four 100-ml portions of pentane. The combine pentane extracts were washed with two 100-ml portions of 5% hydrochloric acid solution, 100 ml of saturated sodium bicarbonate solution and 100 ml of saturated sodium chloride solution and dried. Removal of the pentane by flash evaporation gave 1.7 g of crude product. Glpc analysis showed 52% **29** and 48% of 1-isopropenyl-2,3,3,4,4-pentamethylcyclobut-1-ene (**32**): ir 3.20 (=CH), 6.06 (C=C), 6.22 (C=C) and 11.4 μ (C=CH$_2$, strong); 100 MHz nmr τ 9.02 (s, 6), 8.87 (s, 6), 8.30 (s, 3), 8.13 (s, 3), 5.31 (m, 1), and 5.26 (m, 1); uv max (hexane) 243 mμ (ε 19,000); mass spectrum with a molecular ion at *m/e* 164.1562 (Calcd for $C_{12}H_{20}$: 164.1565).

Pyrolysis of 32.—A 1.0-g sample of **32** was pyrolyzed on the vacuum pyrolysis system at 360° and 0.25 mm to give 0.91 g of crude product. Glpc analysis and preparative collection showed sample to be 96% **21** and 4% **32**.

Pyrolysis of 29.—A 168-mg sample of **29** was pyrolyzed on the vacuum pyrolysis system at 460° and 0.25 mm to give 160 mg of crude product. Glpc analysis showed 72% **21**, 4% **29**, and five other minor unidentified components.

Pyrolysis of 21.—A 66-mg sample of **21** was pyrolyzed on the vacuum pyrolysis system at 580° and 0.25 mm to give 55 mg of crude product. Glpc analysis showed 17% **21**, 50% *p*-xylene, 33% *o*-xylene, and four other unidentified minor products.

An apparatus consisting of a vacuum pyrolysis system followed by a Dry Ice trap and liquid nitrogen trap connected together in series was used to analyze the low-molecular-weight gaseous products. A 71-mg sample of **21** was pyrolyzed at 620° and 0.15 mm using the above system. Glpc analysis of the product in the Dry Ice trap showed **21**, *p*-xylene, and *o*-xylene in the ratio of 1:6:4 along with a number of minor products. Analysis of the products in the liquid nitrogen trap by infrared and mass spectral analysis showed propylene as the major product along with a substantial amount of ethylene.

Registry No.—**6**, 13831-98-6; **7**, 13303-33-8; **8**, 13303-32-7; **15**, 24730-83-4; **16**, 25914-01-6; **17**, 25914-02-7; **20**, 24730-82-3; **21**, 24730-81-2; **22**, 25914-05-0; **24**, 25914-06-1; **25**, 25914-07-2; **29**, 24730-80-1; **31**, 25914-09-4; **32**, 25914-10-7; **45**, 25914-11-8; **46**, 25914-12-9; **47**, 25914-13-0.

Quinone Methide Chemistry. The Benzylic Oxidative Methoxylation of 2,6-Di-*tert*-butyl-*p*-cresol

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Oxidation of 2,6-di-*tert*-butyl-*p*-cresol (**1**) with excess *active* manganese dioxide and lead dioxide in methanol followed by hydrolysis affords 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**5**, 72%) and methyl 3,5-di-*tert*-butyl-4-hydroxybenzoate (**7**, 47%), respectively. Evidence for the intermediacy of quinone methides in these reactions has been obtained by the isolation and characterization of the methanol addition products **3**, **4**, and **6**. A mechanism for metal oxide oxidations of **1** in methanol is presented.

A major subject of investigation of the chemistry of 2,6-di-*tert*-butyl-*p*-cresol (**1**) has been the mechanism of oxidation.[1,2] A substantial understanding of the oxidation of **1** in aprotic solvents has been achieved.[1b,c] However, the oxidations of **1** in protic media have not been as intensively studied. We have now undertaken a product study of the oxidations of **1** in methanol with two commonly used inorganic phenol oxidants, lead dioxide and *active* manganese dioxide.[1b]

Results

A. Manganese Dioxide.[3]—The reaction of **1** with manganese dioxide in a 1:10 weight ratio[4] in methanol at 25° for 72 hr gave, after hydrolysis, a 72% yield of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**5**). A minor product of this reaction, detected to be present to about 5% by vpc, was methyl 3,5-di-*tert*-butyl-4-hydroxybenzoate (**7**). The oxidation of **1** (see Table I) with an equal weight of oxidant was found to give a moderate yield of 2,6-di-*tert*-butyl-α-methoxy-*p*-cresol (**3**). Subsequent reaction of **3** with an equal weight of the oxidant in methanol led to 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde dimethyl acetal **4** in 37% yield. The acetal displayed moderate stability and could be purified by recrystallization from hexane. However, upon standing at room temperature for extended periods, the acetal slowly hydrolyzed to the corresponding aldehyde **5**. Further complete oxidation of **4** in methanol with this oxidant in a 1:5 weight ratio finally gave trimethyl 3,5-di-*tert*-butyl-4-hydroxyorthobenzoate (**6**) in 13% yield. An independent synthesis of **6** by the classical method of Pinner[6] employing 3,5-di-*tert*-butyl-4-hydroxybenzonitrile was not successful since the intermediate methyl 3,5-di-*tert*-butyl-4-hydroxybenzimidate was stable to further methanolysis.

B. Lead Dioxide.—Whereas the oxidation of **1** with

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[1] (a) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957), and references cited therein. (b) H. Musso, *Angew. Chem. Int. Ed. Engl.*, **2**, 723 (1963), and references cited therein. (c) E. R. Altwicker, *Chem. Rev.*, **67**, 475 (1967), and references cited therein. (d) L. V. Gorbunova, N. S. Valileiskaya, M. L. Khidekel, and B. A. Razuvaev, *J. Org. Chem. USSR*, **2**, 1227 (1966). (e) J. Sugita, *Nippon Kagaku Zasshi*, **87**, 1082 (1966); *Chem. Abstr.*, **66**, 9477w (1967). (f) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **89**, 5619 (1967). (g) C. M. Orlando, Jr., *J. Org. Chem.*, **33**, 2516 (1968). (h) H.-D. Becker, *ibid.*, **34**, 1203 (1969).

[2] H.-D. Becker, *ibid.*, **30**, 982 (1965).

[3] Hereafter, manganese dioxide will be used in the text to represent *active* manganese dioxide.

[4] In manganese dioxide oxidations, the quantity of oxidant employed is generally in considerable excess of the substrate since only part of the oxygen in this metal oxide is available for oxidation.[5]

[5] H. B. Henbest and A. Thomas, *J. Chem. Soc.*, 3032 (1957).

[6] Examples of the application of the Pinner method in synthesis of orthobenzoates have been described: H. Kwart and M. B. Price, *J. Amer. Chem. Soc.*, **82**, 5123 (1960).