Synthesis of 2,2-Dimethylhydrazinoacetaldehyde Dimethylhydrazone (8). Chloroacetaldehyde (7.85 g, 0.1 mol) (prepared from the acetal and anhydrous oxalic acid[28]) was cooled to −20° and 29 g (0.4 mol) of 1,1-dimethylhydrazine, previously dried several days with calcium hydride, was added. An exothermic reaction was observed on mixing the reagents. The mixture was kept for 14 hr at 0° and for 4 hr at room temperature. It was then cooled in ice and treated with concentrated sodium hydroxide solution and ether. A stable three-layer system was produced. The ether layer was separated and the remainder was thoroughly extracted with ether. The ether extract was dried with sodium hydroxide and the ether was removed by evaporation at room temperature. The residue (7.63 g) consisted (glpc) of 80% of a mixture of **8** and **2** in a molar ratio of 1:1.66 and 20% of a mixture of starting materials and several minor components. That is, the yields were 15.9% **8** and 26.4% **2**, which presumably arose from **8** during the process. Both **8** and **2** were isolated by preparative glpc.

The product **8**, a colorless liquid, was unstable and darkened on standing. Combustion analysis was considered impractical. Its nmr spectrum was identical with that of the product C isolated from the reaction of **1** with acids (see Results and Discussion). The ir spectrum (also identical with that of C) showed the bands expected for the assigned structure:[6,24] 3380 (w, broad), 2937 (s), 2850 (s), 2810 (s), 2760 (s), 1609 (mw), 1554 (vw), 1467 (s), 1452 (s), 1402 (vw), 1370 (w), 1325 (m), 1260 (s), 1179 (m), 1164 (mw), 1137 (m), 1111 (w), 1094 (mw), 1041 (s), 1013 (vs), 961 (vw), 882 (mw), 834 (mw), and 814 (ms) cm^{-1} (neat, film between NaCl plates).

A mass spectrum of **8**, direct from the gas chromatograph, was obtained with a Varian MAT-CH5 instrument, coupled with an Aerograph 1700 gas chromatograph. The spectrum, obtained at 70 eV, did not exhibit the molecular ion, but showed principal peaks at *m/e*: 129 (8%, $M - CH_3$?), 86 (22%), 85 (27%), 84 (7%), 83 (14%), 71 (10%), 58 (100%, base, Me_2N_2?), 57 (6%), 46 (7%), 44 (33%, Me_2N?), 43 (11%), 42 (47%), 30 (9%), 28 (7%), 27 (5%). The spectrum at *m/e* below 55 was very similar to that of **2**.

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[28] H. Meerwein in "Neuere Methoden der Organische Chemie," Houben-Weyl, Vol. 6/3, Georg Thieme Verlag, Stuttgart, 1965, p 275.

The Palladium Chloride Catalyzed Cyclodimerization of 1-Methylcyclopropene

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Abstract: 1-Methylcyclopropene undergoes a thermal oligomerization in the presence or absence of free-radical inhibitors. The dimeric products of this reaction are shown to be those expected from an "ene" reaction. In the presence of a variety of palladium compounds, a facile cyclodimerization predominates, yielding a mixture of dimethyltricyclo[3.1.0.$0^{2,4}$]hexanes. The latter reaction is also shown by 1,3,3-trimethylcyclopropene, but not by 1,2-dimethylcyclopropene, cyclobutene, norbornadiene, or *trans*-cyclooctane. The mechanistic implications of the catalyzed cyclodimerizations are discussed.

Transition metal catalyzed cycloadditions are an interesting and important branch of organometallic chemistry.[1] The number of catalyzed reactions of simple olefins which yield four-membered rings, however, is quite limited, and the examples known apparently arise from diverse mechanisms. Butadiene gives 1,2-divinylcyclobutane with a bis(cyclooctadiene)-nickel–tris(*o*-phenylphenyl) phosphite catalyst by way of a bis-π-allylnickel intermediate which can close to either a four-, six-, or eight-membered ring.[2] Norbornadienes give pentacyclo[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradecanes with a wide variety of transition-metal catalysts.[3] Allene is dimerized to dimethylenecyclobutanes by nickel phosphine catalysts.[4]

Acetylenes can be catalytically dimerized to cyclobutadienes, trimerized to benzenes, or tetramerized to cyclooctatetraenes depending on the exact nature of the system.[5]

Four-membered ring intermediates have been suggested for the metathesis of both olefins[6,7] and acetylenes[8] using tungsten catalysts. It has been suggested that bond reorganization leads to an excited state of the cyclobutane which can revert to either of the two pairs of isomeric olefins or acetylenes. No cyclobutanes have actually been isolated from these reactions however.

The action of Lewis acids on 2-butyne leads to the

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* To whom correspondence should be addressed.

[1] See G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, **91**, 3800 (1969), and references cited therein.

[2] P. Heimbach and W. Brenner, *Angew. Chem., Int. Ed. Engl.*, **6**, 800 (1967).

[3] For a review, see G. N. Schrauzer, *Advan. Catal.*, 18, 377 (1968).

[4] F. V. Hoover and R. V. Lindsey, Jr., *J. Org. Chem.*, **34**, 3051 (1969).

[5] For a review of transition metal–acetylene chemistry, see F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, 3, 227 (1968).

[6] R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, 3, 170 (1964); L. F. Heckelsberg, R. L.Banks, and G. C. Bailey, *ibid.*, 7, 291 (1968).

[7] N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, 90, 4133 (1968).

[8] F. Pennella, R. L. Banks, and G. C. Bailey, *Chem. Commun.*, 1548 (1968).

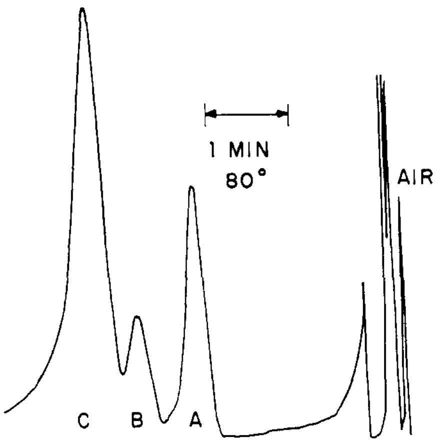


Figure 1. Gas chromatogram of the dimer region of the thermal oligomerization products from methylcyclopropene.

formation of oligomers containing four-membered rings.[9-11]

We present here observations on the palladium-catalyzed cyclodimerization of 1-methylcyclopropenes.

Results

1-Methylcyclopropene was prepared essentially by the method of Fisher and Applequist[12] and purified by a rapid fractional distillation through a packed column at atmospheric pressure. The product was found by gas chromatography to contain *ca.* 2% methylenecyclopropane as the only significant impurity. The methylenecyclopropane was found to be inert in the transformations described below.

If 1-methylcyclopropene was allowed to stand in the condensed phase for any length of time, a mixture of products with a considerably higher boiling point was formed. This decomposition commenced within minutes at room temperature in the neat liquid and was observable within hours at −78° or in more dilute solutions at room temperature. The presence of a wide variety of free-radical inhibitors including phenothiazine, hydroquinone, *N*-nitrosodiphenylamine, *o*-methoxyphenol, 2,5-di-*tert*-butylquinone, and 2,2-diphenylpicrylhydrazyl had no effect on this transformation. The product from the thermal decomposition of methylcyclopropene consisted of an oil, most of which could be molecularly distilled at 0.1 mm and 100°. About 18% of this oil exhibited retention times consistent with dimeric products, at least three components being observed in this region. A typical gas chromatogram of the thermal dimerization product is shown in Figure 1. The only material which could be cleanly separated on a preparative scale (peak A, *ca.* 5% yield based on methylcyclopropene) possessed a C=C stretching frequency of 1629 cm^{-1}. The nmr spectrum of **1** shown in Figure 2 consists of two olefinic hydrogens at δ 7.10, two methyl groups, a singlet at δ 1.17 and a doublet, $J = 5$ Hz, at δ 0.94, and four high-field cyclopropyl absorptions. The infrared frequency corresponds to that of 1,2-unsubstituted cyclopropenes, and the chemical shift of the vinyl protons is also consistent with an unsubstituted cyclopropene double bond.[13] The only dimeric structure consistent with the above evidence is **1** which could be reasonably formed by the sterically favored ene reaction[14] of two 1-methylcyclopropene molecules.

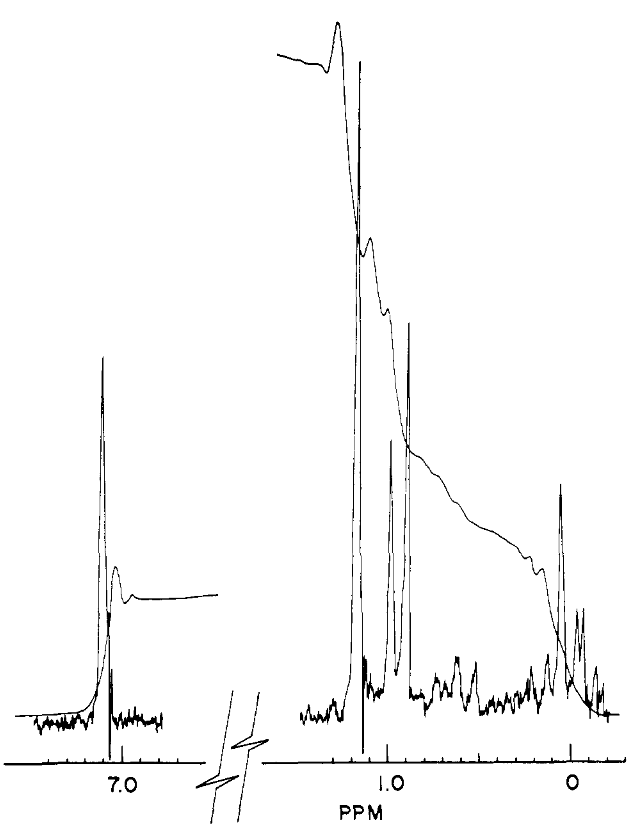
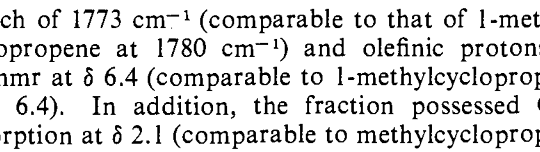


Figure 2. 60-MHz nmr spectrum of methylcyclopropene ene dimer **1**.



A

1

The other two materials of dimeric retention time could not be separated but were collected and examined together. This fraction exhibited an infrared C=C stretch of 1773 cm^{-1} (comparable to that of 1-methylcyclopropene at 1780 cm^{-1}) and olefinic protons in the nmr at δ 6.4 (comparable to 1-methylcyclopropene at δ 6.4). In addition, the fraction possessed CH_3 absorption at δ 2.1 (comparable to methylcyclopropene at δ 2.1). On the basis of this evidence, these materials are presumed to be ene dimers **2** and **3** which would be formed from configurations A′ and B.

When 1-methylcyclopropene is treated with catalytic amounts of palladium dichloride, either neat or in

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(9) 3,4-Dichlorotetramethylcyclobutene, R. Criegee and A. Moschal, *Chem. Ber.*, **92**, 2181 (1959).

(10) Hexamethyl Dewar benzene, W. Schäfer, *Angew. Chem., Int. Ed. Engl.*, **5**, 669 (1966).

(11) (a) Octamethyl-*syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene, H. Hart and L. R. Lerner, *Tetrahedron*, **25**, 813 (1969); (b) K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965); K. Griesbaum, *ibid.*, **86**, 2301 (1964).

(12) F. Fisher and D. E. Applequist, *J. Org. Chem.*, 30, 2089 (1965).

(13) G. L. Closs, *Advan. Alicyc. Chem.*, **1**, 94, 96 (1966).

(14) P. Dowd and A. Gold have recently reported the ene dimerization of cyclopropene itself: *Tetrahedron Lett.*, 85 (1969); for a recent review of the ene reaction, see H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

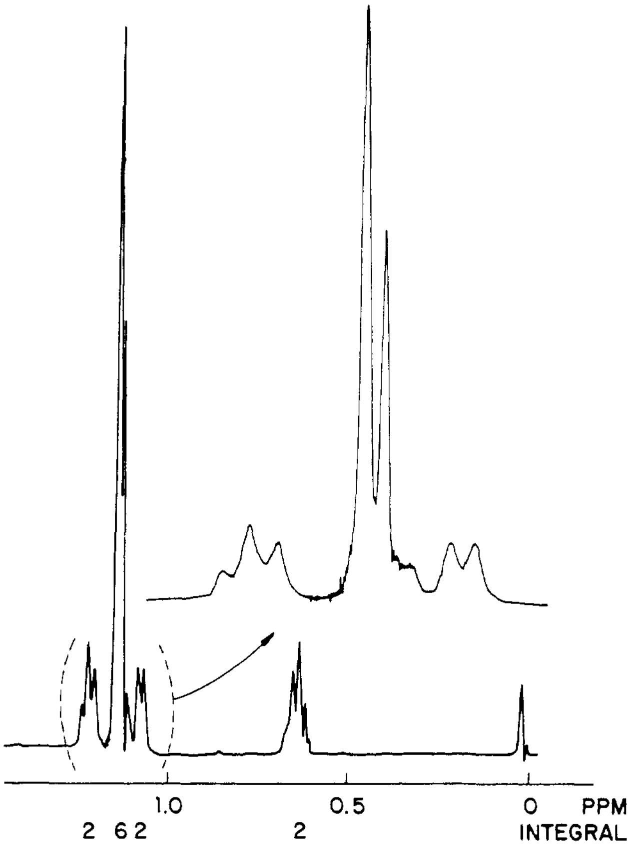
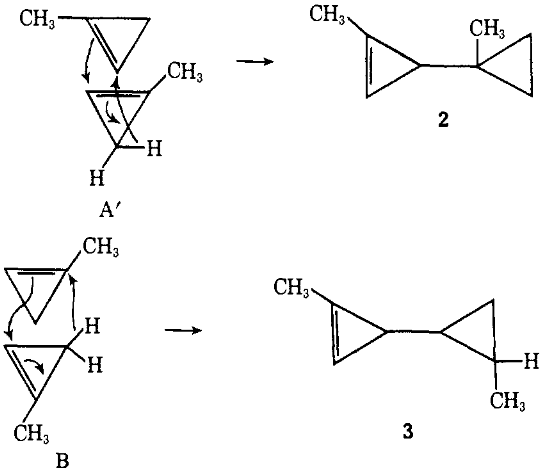


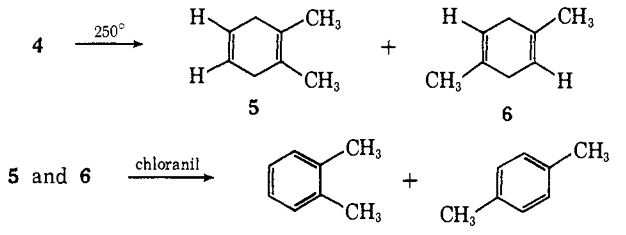
Figure 3. 220-MHz spectrum of methylcyclopropene cyclo dimer **4**.

solution, a vigorous exothermic reaction occurs which is complete in several minutes at 0° and can cause sealed ampoules to explode if carried out at room temperature or above. Aside from small amounts of nonvolatile material, the only reaction product, **4**, possesses the same retention time as **1** on several gas chromatography columns. Unlike **1**, however, **4** possesses no olefinic hydrogens in the nmr and, in fact, the entire spectrum appears at δ <1.35. Although **4** is eluted as a single peak, the 220-MHz nmr spectrum and further chemical transformations described below suggest that it is in fact a mixture of two isomers. The infrared spectrum shows a cyclopropyl CH_2 stretching vibration at 3030 cm^{-1} and no significant absorption in the region 2800–1600 cm^{-1}. The 220-MHz spectrum of **4** is shown in Figure 3 and the presence of two methyl peaks in the ratio of 2:1 suggests the presence of two isomeric dimethyltricyclo[3.1.0.0^{2,4}]hexanes. The mass spectrum of **4** exhibits a parent mass of 108 which is correct for a dimer of methylcyclopropene.

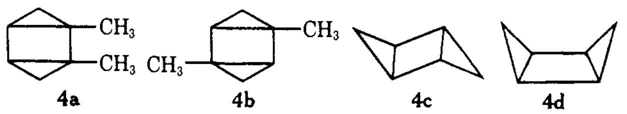


Pyrolysis of **4** in a degassed sealed tube at 250° yielded a 2:1 mixture of two alkenes. The nmr spectrum was consistent with a 2:1 mixture of 1,2-dimethylcyclohexa-1,4-diene (**5**) and 1,4-dimethylcyclohexa-1,4-diene (**6**).

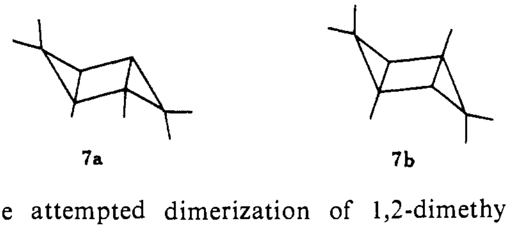
The pyrolysis product shows "singlets" at δ 1.60 and 2.53 and two well-separated vinyl absorptions at δ 5.32 and 5.59 in the ratio of 1:2. These correspond well to the resonance positions of the vinyl protons in cyclohexene (δ 5.57) and 1-methylcyclohexene (δ 5.32).



Finally, the dehydrogenation of the mixture of **5** and **6** with *o*-chloranil at 70° yielded *o*- and *p*-xylene in the ratio of 2:1 as the only products. No *m*-xylene could be detected. These experiments suggest the structure of **4** as a mixture of head-to-head and head-to-tail cyclodimers **4a** and **4b**. For steric reasons, the anti structures **4c** are preferred over the syn structures **4d**, although no concrete evidence for this assignment was obtained.



Dimerization of 1,3,3-trimethylcyclopropene, which unlike 1-methylcyclopropene is stable at 25° in the absence of catalysts,[15] was effected by π-allylpalladium chloride under conditions similar to those used for 1-methylcyclopropene. The products from this reaction were identical with the known photodimers **7a** and **7b** reported by Stechl[16] which have been assigned the *anti*-tricyclohexene structures.



The attempted dimerization of 1,2-dimethylcyclopropene under comparable conditions yielded only the polymer which by nmr possessed a ring-opened structure.

The reaction of some other strained hydrocarbons with dichlorobis(benzonitrile)palladium(II) has led to

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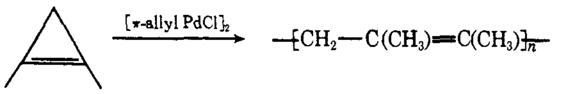
[15] G. L. Closs, L. E. Closs, and W. A. Böll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963).

[16] H. M. Stechl, *Chem. Ber.*, 97, 2681 (1964).



the stoichiometric formation of complexes containing ring-opened ligands.[17]

Neither bicyclobutane nor cyclobutene was oligomerized in the presence of palladium complexes under conditions which oligomerized cyclopropenes. *trans*-Cyclooctene, an olefin with considerable internal strain, was isomerized to *cis*-cyclooctene in the presence of palladium dichloride, but no oligomerization was seen. Norbornene yielded no dimer in the presence of π-allylpalladium chloride.

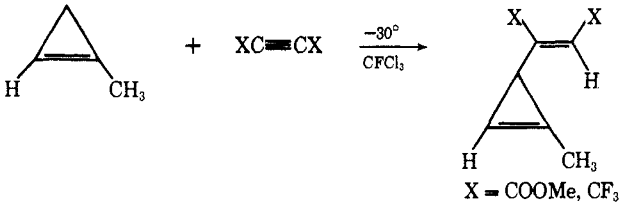
Because of the small amounts of catalyst used in the reaction and the formation of polymeric by-products, it was not possible to isolate the palladium-containing material at the end of the reaction. In several runs the walls of the reaction vessel were coated with what appeared to be a palladium mirror, so it is assumed that this is at least one mode of catalyst deactivation. Approximately 250 catalyst cycles were achieved with both 1-methylcyclopropene and 1,3,3-trimethylcyclopropene as substrates and using several palladium compounds as catalysts.[18] Active palladium salts included the chloride, bromide, iodide, nitrate, π-allylpalladium chloride, and dichlorobis(benzonitrile)palladium(II). Because of its greater solubility in organic solvents the π-allyl complex was the most convenient catalyst.

Palladium-on-charcoal and palladium sulfide did not catalyze the dimerization, but they may have failed because of low solubility if the reaction is in fact homogeneous. *Most importantly, dichlorobis(triphenylphosphine)palladium(II) did not catalyze the dimerization and could be recovered unchanged after the thermal oligomerization products from the cyclopropene were removed.*

Chlorides of platinum(II), osmium(III), ruthenium(III), rhodium(III), or rhenium(V) produced no significant amount of[19a] cyclodimer. If methylcyclopropene was heated rapidly to room temperature in the presence of molybdenum hexacarbonyl, some cyclodimer **4** was formed,[19b] accompanied by thermal oligomerization, although at 0° no **4** was obtained. These experiments do not preclude the formation of **4** under other conditions, as evidenced by the temperature sensitivity of the formation of **4** by molybdenum hexacarbonyl.

Solvent does not appear to be a relevant variable in this reaction. Methylcyclopropene has been successfully dimerized in toluene, pentane, hexane, trichlorofluoromethane, tetrahydrofuran, ether, ethanol, and methylene chloride, in the presence and absence of air.

Study of possible catalyzed reactions of 1-methylcyclopropene with sufficiently reactive acetylenes was precluded by a very facile ene reaction. Thus, hexafluorobutyne and dimethyl acetylenedicarboxylate at −30° were rapidly converted to the ene products with 1-methylcyclopropene, but the products resinified at 25° and were not further identified.[14a]



Discussion

It is readily apparent from strain energy considerations that any oligomerization of cyclopropene should be energetically favorable.[20] In the absence of catalysts, the ene dimerization of cyclopropenes appears to be the kinetically favored process. If one assumes that this process and not the normal free-radical polymerization of alkenes leads to the spontaneous polymerizations of cyclopropenes, several discordant observations fall into place. The failure of free-radical inhibitors to retard the polymerization of 1-methylcyclopropene and the high stability of 3,3-dimethylcyclopropene as opposed to those with at least one hydrogen in the 3 position[15] are best rationalized by this oligomerization mechanism.

In the presence of palladium catalysts, the course of the oligomerization is diverted to a cyclodimerization. The experiments which shed the greatest light on the mechanism of the catalyzed dimerization are the reactions of 1-methylcyclopropene with molybdenum hexacarbonyl and dichlorobis(triphenylphosphine)palladium(II). In both cases, the response of 1-methylcyclopropene to the catalyst mirrors the behavior of 2-butyne in the acetylene trimerization reaction.

The transition metal catalyzed trimerization of 2-butyne has recently been studied in detail by Whitesides[1] who suggested an intermediate tetramethylcyclobutadiene complex may be involved in the reaction of 2-butyne with dichlorobis(benzonitrile)palladium(II) chloride. Further reaction with another mole of 2-butyne leads to hexamethylbenzene, but with diarylacetylenes, under the proper conditions, cyclobutadiene-palladium complexes may be isolated.[21-23] The acetylene substituents can direct the course of the palladium-promoted oligomerization to either dimerization or trimerization. In this respect, the tricyclohexanes **4** and **7** may be considered as "bishomocyclobutadienes." The stoichiometric formation of cyclobutadiene complexes but catalytic formation of free tricyclohexanes can be understood in terms of the strong π bonding of the cyclobutadiene ligand. Because of the much weaker interaction of bishomocyclobutadiene, additional cyclopropene is able to displace the tricyclohexane from the coordination sphere of the palladium and thus make the reaction catalytic. Mango and Schacht-

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(17) (a) 1,2,3-Triphenylcyclopropene, P. Mushak and M. A. Battiste, *J. Organometal. Chem.*, 17, P46 (1969); (b) methylenecyclopropane, R. Noyori and H. Takaya, *Chem. Commun.*, 525 (1969); (c) spiropentane, A. D. Ketley and J. A. Braatz, *ibid.*, 959 (1968); (d) vinylcyclopropane, T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, 33, 876 (1968).

(18) Although the trimerization of 2-butyne by dichlorobis(benzonitrile)palladium(II) is described as catalytic[1] (W. I. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964)), there is no evidence for more than one "catalyst cycle."

(19) (a) Because the retention time of **4** is identical with **1** and thermal oligomers were formed in all cases where catalysis leading to **4** was not particularly effective, small amounts of cyclodimer would not be detected by gas chromatography. (b) We wish to thank Dr. J. C. Kauer for this experiment.

(20) K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, **84**, 3980 (1962).

(21) P. M. Maitles, D. F. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, **43**, 470 (1965).

(22) R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965).

(23) R. Hüttel and H. J. Weugebauer, *Tetrahedron Lett.*, 3541 (1964).

schneider have presented arguments based on orbital symmetry considerations that the thermal, metal-catalyzed cyclodimerization of olefins should be a concerted reaction,[24] while the cyclodimerization of acetylenes should be stepwise or binuclear.[25] Exactly how the cyclopropenes fit into this scheme is unclear, except that this reaction seems to be more typical of acetylenes than olefins and therefore if the course of the reaction is, in fact, governed by symmetry considerations, the reaction may be stepwise or binuclear.

There is both theoretical and experimental evidence that cyclopropenes and acetylenes have similar electronic structures and physical properties.[26]

By analogy with the palladium-catalyzed ethylene dimerization,[27] norbornene polymerization,[28] and acetylene trimerization,[29a,b] the mechanism may involve separate insertion and elimination reaction steps.

Unanswered is the critical question of the process involved in carbon–carbon bond formation (with ring closure in this case). In the absence of experimental evidence, we prefer not to speculate further.

Experimental Section[30]

Materials. 1-Methylcyclopropene was prepared by the method of Fisher and Applequist.[12] 1,3,3-Trimethylcyclopropene was prepared by the method of Closs, *et al.*[15] 1,2-Dimethylcyclopropene was prepared by methylation of the anion of 1-methylcyclopropene analogous to the preparation of 1,3,3-trimethylcyclopropene-2-carboxylic acid by Closs.[31] Palladium salts were obtained from Alfa Chemical Company. π-Allylpalladium chloride was prepared by the method of Dent, Long, and Wilkinson.[32] Dichlorobis(benzonitrile)palladium(II) was prepared by the method of Kharasch.[33]

Attempted Stabilization of 1-Methylcyclopropene. Separate nmr tubes were filled with 0.30-ml aliquots of 1-methylcyclopropene and 5 mg of phenothiazene, hydroquinone, *N*-nitrosodiphenylamine, *p*-methoxyphenol, 2,5-di-*tert*-butylquinone, and 2,2-diphenylpicrylhydrazyl, respectively. These tubes were degassed, sealed, and allowed to stand at room temperature for 64 hr in subdued light. At the end of this time, the nmr showed no 1-methylcyclopropene and the spectra were essentially identical with that of an "unstabilized" sample of 1-methylcyclopropene. A similar sample kept at liquid nitrogen temperature was unchanged during this interval.

Oligomerization of 1-Methylcyclopropene. In a heavy-walled Carius tube was placed 5 ml of trichlorofluoromethane. After degassing under vacuum, 7.7 g of 1-methylcyclopropene was distilled into the tube. The mixture was degassed again and the tube was sealed under vacuum. The tube was allowed to stand at room temperature for 5 days, cooled to 0°, and opened. The solvent was evaporated and the residue molecularly distilled at reduced pressure to yield *ca.* 8.5 ml of liquid. A gas chromatogram is shown in Figure 1. The yield of peak A is 5% and the combined yield of B and C is 13%. A small amount of peak A was preparatively collected.

The product showed the following characteristics: ir 2950, 1629, and 1008 cm^{-1}; nmr δ 7.10 (quartet, $J = 0.7$, $=\mathrm{C}H$), 1.17 (doublet, $J = 0.7$, $\mathrm{C}H_3$), 0.94 (doublet, $J = 5$, $\mathrm{CHC}H_3$), 0.9–0.5 (multiplet, 2 H), 0.0 (multiplet, 2 H). Peaks B and C were collected together: ir 2990, 2950, 2915, 2874, 1773, 1558, 1070, 1042, and 1022 cm^{-1}; nmr δ 6.4, 2.1, and cyclopropyl absorptions above 1.0.

Because of low yields and the unstable nature of the above products, it was not possible to obtain analytical data in the usual sense.

Catalyzed Dimerization of 1-Methylcyclopropene. A mixture of 5 ml of spectrograde hexane and 5 mg of palladium dichloride was placed in a thin-walled Carius tube and degassed under vacuum. Then *ca.* 3 ml of 1-methylcyclopropene was distilled into the tube and the tube sealed under vacuum. The tube was mechanically agitated as it warmed to room temperature. In the absence of stirring or agitation, the tubes often exploded because of excessive local heating. Initially, the tube was maintained at room temperature for 18 hr, but subsequent experiments indicated the reaction was complete in minutes. At the end of the reaction period, the tube was cooled and opened. The slurry obtained was centrifuged and the clear solution was rapidly distilled to remove any palladium-containing residues and then redistilled through a short spinning-band column to give 0.55 g of dimethyltricyclo[3.1.0.0^{2,4}]hexanes (**4**), bp 87–91°.

Anal. Calcd for $(C_4H_6)_n$: C, 88.8; H, 11.2. Found: C, 89.0, 89.1; H, 10.8, 11.2.

The mass spectrum showed a molecular ion at *m/e* 108 and a base peak at 93 (M − 15); nmr ($CDCl_3$–TMS) δ 1.22 (two doublets in the ratio of 1:2 separated by 0.02 ppm, $J = 3$ Hz, $\mathrm{C}H$), 1.13 (2 singlets in the ratio of 2:1 separated by 0.015 ppm, $\mathrm{C}H_3$), 1.00 (doublet, $J = 3$ Hz, $\mathrm{C}H_2$ endo), 0.63 (multiplet, $\mathrm{C}H_2$ exo).

Thermal Rearrangement of the Cyclodimer 4. An nmr tube of cyclodimer **4** was degassed, sealed under vacuum, and then heated at 250° for 2 hr. The nmr spectrum showed the complete absence of starting material and the following new absorptions: δ 5.59 (narrow multiplet) and 5.32 (broad multiplet, combined area 2 H, $=\mathrm{C}H$), 2.53 (broad singlet, 4 H, $\mathrm{C}H_2\text{—C=C}$), 1.60 (singlet with shoulder, 6 H, $\mathrm{C}H_3\text{—C=C}$).

The material was imperfectly separated into two peaks by gas chromatography at 96° with retention times of 6.5 and 7.1 min in the area ratio of 1:2.

Dehydrogenation of Cyclohexadienes 5 and 6. A sample of 0.06 g of the mixture of cyclohexadienes **5** and **6** was treated with 2.0 ml of benzene and 0.137 g of *o*-chloranil. The red color of the latter disappeared immediately, a small additional amount of *o*-chloranil was added, and the solution was heated at 70° for 5 min. At the end of the reaction, the solution was filtered through a small column of neutral alumina and examined by gas chromatography. The gas chromatogram showed two peaks identical with *o*- and *p*-xylene in the ratio of 2:1. No peak was observed for *m*-xylene. The nmr spectrum confirmed the presence of a 2:1 mixture of *o*- and *p*-xylene by the presence of two methyl peaks at δ 2.03 and 2.14.

Catalyzed Dimerization of 1,3,3-Trimethylcyclopropene. About 1 g of 1,3,3-trimethylcyclopropene was treated with catalytic amounts of π-allylpalladium chloride in toluene at −30°. The reaction was monitored by gas chromatography, and when no further change occurred (less than 1 hr), the solvent was removed by distillation through a short spinning-band column and the residue isolated by preparative gas chromatography at 80°, yield 100 mg. The nmr spectrum of this material was identical with that reported by Stechl[16] for the photolytically produced cyclodimer.

Anal. Calcd for $(C_8H_{10})_n$: C, 87.72; H, 12.3. Found: C, 87.8; H, 12.3.

The molecular weight determined by mass spectroscopy is 164, consistent with a dimer. The infrared spectrum showed strong bands at 2994, 2963, 2924, 2870, 1456, 1439, and 1366 cm^{-1}. The nmr spectrum showed the following resonances (all singlets): δ 1.20, 1.18 (6 H), 1.11, 1.09 (6 H), 1.00, 0.97 (2 H), 0.88 (6 H). The nmr spectrum is consistent with a 1:1 mixture of **7a** and **7b**.

Reaction of 1-Methylcyclopropene with Metal Chlorides. Into separate serum-capped vials were placed 10 mg of platinum(II) chloride, ruthenium(III) chloride, rhodium(III) chloride, and rhenium(V) chloride. The vials were charged with 1 ml of pentane solvent and degassed by freeze–pump–thaw cycles. Approximately 500 mg of 1-methylcyclopropene was distilled into the vials and they were allowed to warm first to −78° and then to 0° with stirring behind a safety shield. Periodic investigation of the contents by gas chromatography revealed only the characteristic pattern thermal dimerization as shown in Figure 1.

Reaction of 1,2-Dimethylcyclopropene with Palladium Complexes. To 50 ml of 1,2-dimethylcyclopropene in 1 ml of ether was added

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[24] F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2483 (1967).

[25] F. D. Mango and J. H. Schachtschneider, *ibid.*, **91**, 1030 (1969).

[26] W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).

[27] Y. Kusanaki, R. Katsuno, N. Hasegawa, S. Kurematsu, Y. Nagao, K. Ishii, and S. Tsutsumi, *Bull. Chem. Soc., Jap.*, **39**, 2021 (1966).

[28] R. G. Schultz, *Polym. Lett.*, **2**, 541 (1966).

[29] (a) H. Dietl, H. Reinheimer, J. Moffatt, and P. M. Maitles, *J. Amer. Chem. Soc.*, **92**, 2276 (1970). (b) For an intramolecular example of this type of a reaction, see T. J. Katz and S. A. Cerefice, *ibid.*, **91**, 6519 (1969).

[30] Infrared spectra were determined on Perkin-Elmer 137 and 237 instruments. Nmr spectra were recorded in carbon tetrachloride solution with tetramethylsilane as internal reference in Varian A-60, HA-100, and HR-220 instruments. Gas chromatography, unless otherwise stated, was done with a 6 ft × 1/4 in. column of Dow Silicon 200 on a base of Chromosorb W. Boiling points were uncorrected.

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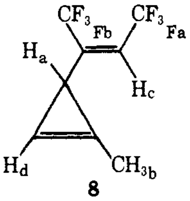
[32] See Dent, *et al.*, ref 18.

[33] M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, **65**, 882 (1938).

10 mg of π-allylpalladium chloride. The solution was stirred at 0° for 2 hr and the cream-colored precipitate which formed was collected by filtration. Nmr examination in benzene solution revealed two resonances at δ 1.71 and 3.08 in the ratio of 6:2 consistent with a ring-opened, polymeric structure.

Thermal Reaction of Methylcyclopropene with Acetylenes. Into a 5-ml serum-capped vial equipped with magnetic stirrer was placed 1 ml of CFCl$_3$. The solvent was degassed on the vacuum line, and *ca.* 1 g of hexafluorobutyne was distilled in followed by *ca.* 1 g of methylcyclopropene. The solution was warmed to −78° and then stirred for 3 hr at −30°. The nmr spectrum of the resulting solution was consistent with structure **8** for the adduct. The reaction occurs explosively if the neat compounds are allowed to warm toward room temperature: nmr (CFCl$_3$–TMS) δ 1.03 (broad singlet, H_a), 2.18 (doublet, J = 1.2 Hz, H_b), 5.54 (quartet, J = 9 Hz, H_c), 6.54 (broad singlet, H_d); ϕ^* = 57.4, quartet, J = 11 of doublets, J = 9 Hz, F_a; ϕ^* = 60.4, quartet, J = 11Hz, F_b. The reaction with dimethyl acetylenedicarboxylate proceeded analogously. The product is assigned the *cis* configuration by analogy with the hexafluorobutyne adduct: nmr (CFCl$_3$–TMS) δ 1.05 (broad, H_a), 2.18 (doublet, J = 1.5, H_b), 3.49, 3.55 (singlets, H_c), 5.7 (singlet, H_d), 6.51 (broad, H_e).



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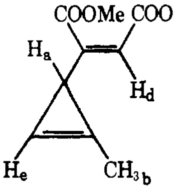

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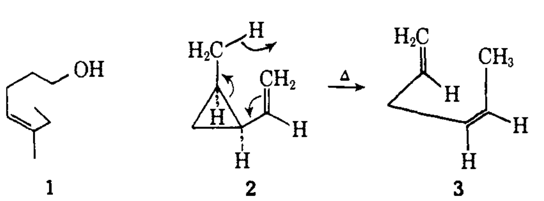
Communications to the Editor

New Stereospecific Synthetic Routes to Trisubstituted Olefins

Sir:

In connection with studies on the stereocontrolled synthesis of C$_{17}$ and C$_{18}$ Cecropia juvenile hormones,[1] a simple stereospecific synthesis of 5-methyl-*cis*-4-hepten-1-ol (**1**) was required.[2] This communication describes two methods for the assembly of olefinic alcohols such as **1** efficiently and with complete specificity.

The first approach is based on the thermal rearrangement defined by the class prototype, *cis*-2-methylvinylcyclopropane (**2**) → *cis*-1,4-hexadiene (**3**).[3–6] In this interesting transformation a stereorelationship about a three-membered ring is translated into a stereorelationship about a carbon–carbon double bond as shown, because the 1,5 hydrogen shift occurs with vinyl methylene oriented approximately s-cis to the cyclopropyl group. Figure 1 outlines the sequence of reactions utilized. *trans*-3-Methylpent-3-en-1-yne, prepared by dehydration of 3-methylpent-1-yn-3-ol using sulfuric acid–acetic anhydride, followed by distillation through a spinning-band column,[7,8] was hydroxymethylated by successive treatment in tetrahydrofuran with *n*-butyllithium (−78°, 30 min) and excess dry paraformaldehyde (−78° initially, then from −78 to 23° and at 23° for 2 hr)[9,10] to give the acetate **4**[11] after acetylation with acetic anhydride–pyridine. Selective hydrogenation of **4** using Lindlar catalyst[12] in benzene containing a small amount of quinoline, followed by saponification using 0.5 *N* methanolic sodium hydroxide, afforded the 2,3-*cis*-4,5-*trans*-dienol **5**[11] in high overall yield from the starting enyne. Addition to a solution of **5** in ether at reflux[10] of an excess of Simmons–Smith reagent[13,14] over a period of 1–2 hr resulted in selective formation of the cis-substituted cyclopropyl carbinol **6**[11] (90% yield). Addition of **6** to a vertical Pyrex column packed with Pyrex helices and maintained at 350° (with a slow current of nitrogen as carrier) yielded a condensate from which the pure aldehyde **7**[11] was readily obtained in 64% yield. No stereoisomeric products could be detected by vapor-phase chromatographic analysis. Reduction of the aldehyde **7** with ethanolic sodium borohydride at 0° produced the corresponding alcohol **1**[11] in 96% yield.



1 **2** **3**

A second synthesis of **1** (see Figure 2) proceeded from the tetrahydropyranyloxy aldehyde **8**,[11a] obtained in 98% yield from 1,4-butanediol monotetrahydropyranyl ether by oxidation with chromium trioxide–pyridine

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(1) See E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 6636 (1970).

(2) For a synthesis of the lower homolog, 4-methyl-*cis*-3-hexen-1-ol (from *p*-cresol) and its application to the synthesis of the C$_{18}$ juvenile hormone, see E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *ibid.*, 90, 5618 (1968).

(3) W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **688**, 28 (1965).

(4) R. J. Ellis and H. M. Frey, *Proc. Chem. Soc., London*, 221 (1964).

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(7) A. F. Thompson, Jr., N. A. Milas, and I. Rovno, *J. Amer. Chem. Soc.*, **63**, 752 (1941).

(8) M. Bertrand and H. Monti, *Tetrahedron Lett.*, 1069 (1968).

(9) A. Schaap, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays Bas*, **84**, 1200 (1965).

(10) Reaction conducted with exclusion of air.

(11) Satisfactory (a) spectroscopic and (b) analytical data were obtained for this intermediate, a colorless liquid.

(12) H. Lindlar and R. Dubuis, *Org. Syn.*, **46**, 89 (1966).

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

(14) Prepared by dropwise addition of methylene iodide to a stirred suspension of zinc–copper couple [E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964)] in ether at reflux.