

was then added, and two 50-ml ether extractions were taken. The extracts were combined and washed with saturated sodium chloride, dried over magnesium sulfate, and decolorized with charcoal. Removal of the ether by rotary evaporation resulted in an oil, whose pmr spectrum was identical with that of the hydroxy olefin 7. Crystallization from pentane-ether gave 0.41 g (93%), mp 188–190°.

Reaction of Trichloromethylphenylcarbinol with Silver Perchlorate in Aqueous Acetone.—To 2.0 g (0.16 mol) of trichloromethylphenylcarbinol³⁷ dissolved in 60 ml of acetone was added 3 equiv (10.0 g) of silver perchlorate in 30 ml of water to form a homogeneous solution. No silver chloride precipitate was observed during a 36-hr period of reflux. Work-up gave only unreacted starting material.

Reaction of DDT with Silver Perchlorate in Aqueous Acetone.—2,2-Bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT, 1 g, 2.8 mmol) in 20 ml of acetone was heated to reflux. To this was added 1.75 g (8.4 mmol) of silver perchlorate in 10 ml of water, and the refluxing was continued for 48 hr. The standard work-up revealed only starting material in the ether layer and only traces of unidentifiable material in the water layer.

Reaction of the Syn Ketone 9 with Silver Perchlorate in Aqueous Acetone.—A solution of 0.20 g (0.54 mmol) of 9 and 0.34 g (16.2 mmol) of silver perchlorate in 20 ml of acetone and 10 ml of water was held at reflux for 48 hr. The reaction was worked up in the usual manner. The ether layer showed that ~10% of the ketone had reacted to give the corresponding olefin (*vide infra*). The aqueous layer yielded no organic material.

Synthesis of Olefins 15 and 16.—Olefins 15 and 16 were synthesized from 10 and 9, respectively, in the same fashion (1 M lithium chloride in DMA at 130°) as in the case of the olefins 25 and 29 (*vide supra*). The olefins were obtained in 80–90% and were recrystallized from ethanol.

The pmr spectrum for the olefin 15 (mp 169°; $\nu_{C=C}$ 1650 cm^{-1} , ν_{OH} 3560 cm^{-1}) shows two singlets (1 H each) at τ 5.15 and 5.36 and a complex multiplet (8 H) from 2.3 to 3.0.

Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{Cl}_3\text{O}$: C, 60.48; H, 3.28. Found: C, 60.24; H, 3.36.

The pmr spectrum of the ketone 16 (mp 200°; $\nu_{C=C}$ 1620 cm^{-1} , $\nu_{C=O}$ 1690 cm^{-1}) shows a singlet (1 H) at τ 4.85 and a complex multiplet (8 H) from 2.2 to 3.0.

(37) Kindly provided by Dr. E. W. Reeve, University of Maryland.

Anal. Calcd for $\text{C}_{17}\text{H}_9\text{Cl}_3\text{O}$: C, 60.84; H, 2.73. Found: C, 60.95; H, 2.81.

Kinetic Procedure.—Dimethylacetamide (reagent grade and twice distilled *in vacuo* from P_2O_5) solution (0.03 M in alkyl halide and 0.308 M in lithium chloride, standardized against silver nitrate by potentiometric titration) was placed in sealed ampoules and heated at 130.2° ($\pm 0.05^\circ$) in a constant temperature silicone oil bath. Samples (5.0 ml) were withdrawn at varying times and quenched in 50 ml of water. The solutions were analyzed by potentiometric titration (Sargent-Welch Model DG recording titrator) against a standardized solution of sodium hydroxide. A plot of log (liberated acid) vs. time gave a straight line, the slope of which was $k_{\text{obsd}}/2.303$. The second-order rate constant (k_2) is $k_{\text{obsd}}/[\text{Cl}^-]$. By variation of [LiCl] from 0.902 to 0.094 M, it was shown that each run gave the same k_2 to within $\pm 10\%$.

Attempts at accurately measuring the rates of reactions of the alkyl halides (0.03 M) with 0.312 M sodium hydroxide in methanol at 65.1° (sealed ampoules) were not successful. Plots of log (liberated Cl^-) vs. time gave fairly straight lines for only ~20–40% reaction times. Rough data on the relative half-lives of the reactions of 18–22 with 0.312 M sodium hydroxide in methanol at 65.1° were obtained by quenching the reactions at ~15, 25, and 40% reaction times and measuring the extent of reaction by pmr spectroscopy. The relative rates for disappearance of starting materials as measured in this fashion follow: hydrocarbon 22 (1.0), methyl ether 21 (0.4), endo alcohol 20 (1.5), exo alcohol 18 (8), ketone 19 (150).

Registry No.—3, 27995-04-6; 4, 27995-05-7; 5, 27948-20-5; 6, 27948-21-6; 7, 34226-23-8; 8, 34226-24-9; 9, 27948-22-7; 10, 34226-26-1; 12, 34226-27-2; 15, 34226-28-3; 16, 34220-44-5; 18, 34226-29-4; 19, 34226-30-7; 20, 34226-31-8; 21, 34226-32-9; 22, 34226-33-0; 23, 34226-34-1; 25, 34226-35-2; 26, 34226-36-3; 27, 34226-37-4; 28, 34220-45-6; 29, 34220-46-7.

Acknowledgment.—Financial support from the donors of the Petroleum Research Fund of the American Chemical Society and from the National Science Foundation is gratefully acknowledged.

Synthetic Routes to Polyspiro Compounds with a Central Cyclobutane Ring

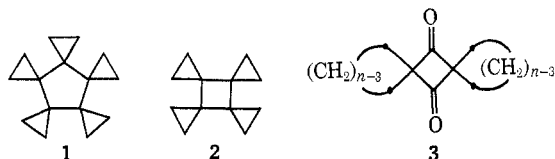
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The reaction of dione 3 ($n = 6$) with triphenylphosphinemethylene in a benzene solution leads to 4 ($n = 6$) in 15–20% yields along with 9 ($n = 6$). On the other hand, 3 ($n = 5$) on treatment with this ylide leads only to the ring-opened product 9 ($n = 5$). Treatment of 6 with dimethylsulfoxonium methylide leads to 12. The diepisulfides 13 and 14 ($n = 5$ or 6) undergo smooth desulfurization on heating with tri-*n*-butylphosphine to yield 7 and 4 ($n = 5$ or 6), respectively, in good yields. The dienes 7 and 4 ($n = 5$ or 6) on treatment with the Simmons-Smith reagent lead to 16 and 5 ($n = 5$ or 6). The trispiroenes 15 ($n = 5$) and 17 were also isolated. The nmr data for the trispiro and tetraspiro systems along with 16 and 17 are presented and briefly discussed.

The synthesis of pentaspiro[2.0.2.0.2.0.2.0]pentadecane (1) has recently been described by Ripoll and Conia.² This was the first report of the preparation of this type of polyspiro system and the general



(1) Ethiopian Fellow of the African Graduate Fellowship Program (AFGRAD).

(2) (a) J. L. Ripoll and J. M. Conia, *Tetrahedron Lett.*, 979 (1969); (b) J. L. Ripoll, J. C. Limasset, and J. M. Conia, *Tetrahedron*, **27**, 2431 (1971).

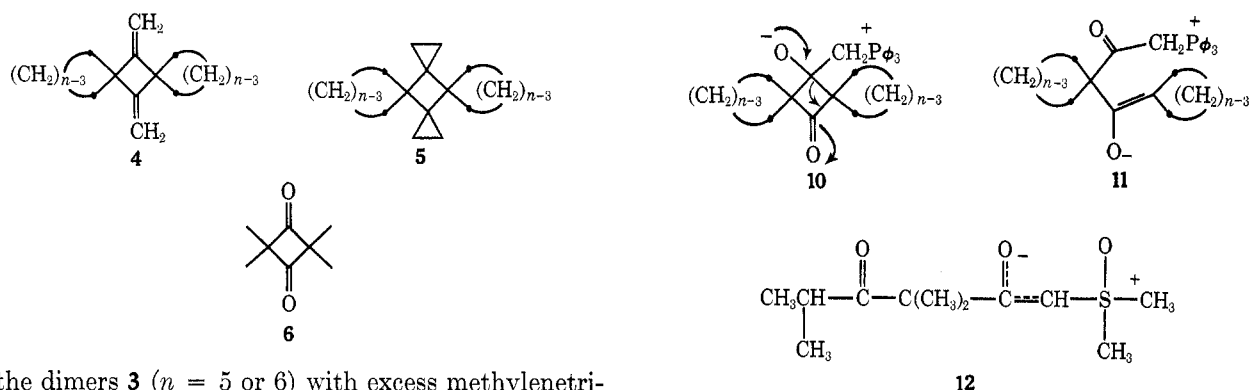
name "rotane" was suggested because of the paddle-wheel-like arrangement of the outer cyclopropane rings. Shortly thereafter, the synthesis of tetraspiro[2.0.2.0.2.0.2.0]dodecane (2) was reported.^{3,4}

We wish to report synthetic routes to "rotanes" possessing an internal four-membered ring flanked by "blades" of varying ring size. The original synthetic scheme centered on the readily available polymethyleneketene dimers 3 ($n = 5$ or 6) as potential starting materials.⁵ It was envisioned that treatment

(3) J. M. Conia and J. M. Denis, *Tetrahedron Lett.*, 3545 (1969).

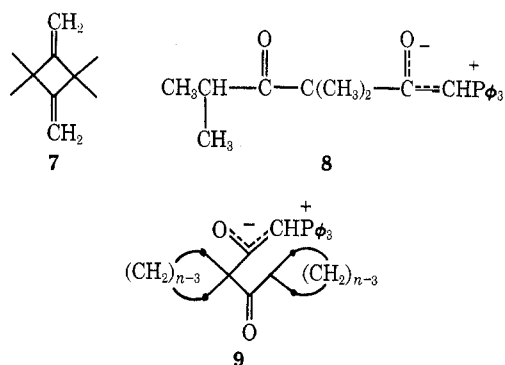
(4) P. Le Perche and J. M. Conia, *ibid.*, 1587 (1970).

(5) J. L. E. Erickson, F. E. Collins, Jr., and B. L. Owen, *J. Org. Chem.*, **31**, 480 (1966).



of the dimers **3** ($n = 5$ or 6) with excess methylenetriphenylphosphorane might lead to **4** ($n = 5$ or 6). These latter compounds could then be converted to the "paddlewheel" systems **5** ($n = 5$ or 6) via the Simmons-Smith procedure.⁶ However, this approach suffers from the problem that ring-opened products generally have been reported in various reactions of tetramethylcyclobutane-1,3-dione (**6**).⁷ For example, treatment of **6** with triphenylphosphinemethylene (methyltriphenylphosphonium bromide and *n*-butyllithium in THF) leads to the ring-opened product **8**.^{7c}

Dione-Ylide Reactions.—Treatment of **6** with 2 equiv of triphenylphosphinemethylene (generated in DMSO from the phosphonium salt and Na^+DMSO^-) led to **8** in 77% yield. No diene **7** could be detected



in the reaction mixture. In a similar manner, **3** ($n = 5$) led to a 75% yield of **9** ($n = 5$). The structure of **9** ($n = 5$) could readily be ascertained by an nmr comparison of its spectrum with that previously reported for **8**.^{7c} When **3** ($n = 5$) was treated with 3 equiv of triphenylphosphinemethylene (generated in benzene from the phosphonium salt using *n*-butyllithium) a 75% yield **9** ($n = 5$) was isolated and no diene was detectable. Nevertheless, dione **3** ($n = 6$) on treatment with excess ylide (2–2.5 equiv prepared from methyltriphenylphosphonium bromide using *n*-butyllithium or potassium *tert*-butoxide in benzene) led to diene **4** ($n = 6$) in 15–20% yields along with the ring-opened ylide **9** ($n = 6$).

Thus in our hands only the dione **3** ($n = 6$) led to poor yields of the desired diene **4** ($n = 6$) while diones **3** ($n = 5$) and **6** led almost totally to the ring-opened products. The ring-opening reaction of an intermediate^{7c} such as **10** ($n = 5$ or 6) would be expected to proceed more readily in the case of $n = 5$ than for $n = 6$.

(6) See A. P. Krapcho and D. E. Horn, *Tetrahedron Lett.*, 4537 (1969), for a preliminary communication.

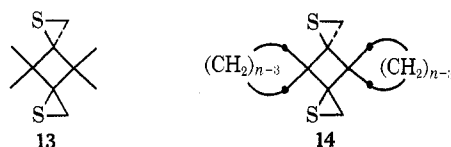
(7) (a) J. L. E. Erickson and G. C. Kitchens, *J. Amer. Chem. Soc.*, **68**, 492 (1946); (b) J. C. Combret, *Ann. Chim. (Paris)*, **4**, 481 (1969); (c) E. A. LaLancette, *J. Org. Chem.*, **29**, 2957 (1964).

Intermediate **10** has less internal angle strain in the central cyclobutanone ring when $n = 6$ than when $n = 5$; hence the ring-opening reaction leading to **11** ($n = 5$) would be expected to proceed more rapidly and dominate the formation of the transient methylene ketone. A nonpolar solvent such as benzene appears to favor the methylene ketone.

It was also of interest to investigate the reaction of the dione **6** with dimethylsulfoxonium methylide.⁸ Treatment of **6** with this reagent led to the ring-opened product **12** in 37% yield. No diepoxide could be isolated in this reaction.

Desulfurizations.—In order to circumvent the facile ring-opening processes exhibited by the 1,3-diones in the Wittig reaction, our attention was next focused on the conversion of the diepulfides **13** and **14** ($n = 5$ or 6) into the corresponding dimethylene systems **7** and **4** ($n = 5$ or 6), respectively. Recently we have prepared the stereoisomeric diepulfides **13** and **14** ($n = 5$ or 6) by treatment of the thiones **6** ($\text{O} = \text{S}$) and **3** ($\text{O} = \text{S}$, $n = 5$ or 6) with diazomethane followed by thermal decomposition of the resulting Δ^3 -1,3,4-thiadiazolines.⁹ On heating the diepulfides in tri-*n*-butylphosphine at 80–100° for 18–36 hr, a smooth desulfurization occurred¹⁰ and the dimethylene systems could be obtained in good yields.

Treatment of the mixture of *cis* and *trans* diepulfides **13** with tri-*n*-butylphosphine (80° for 60 hr)



led to **7** in 67% yield. The compound collected in the condenser and was identical in melting point and nmr spectrum with those of a previously reported sample.¹¹ Treatment of the stereoisomeric mixture of diepulfides **14** ($n = 5$ or 6) with tri-*n*-butylphosphine (100° for 36 and 18 hr, respectively) followed by addition of pentane and chromatography on alumina led to **4** ($n = 5$ or 6) in yields of 73 and 70%, respectively. Compound **4** ($n = 6$) was identical in all respects with the sample prepared by the di-Wittig procedure.

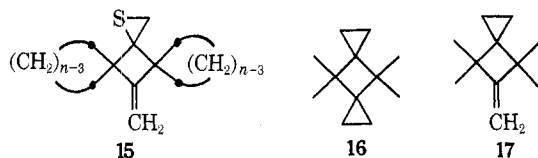
(8) (a) M. Fieser and L. Fieser, "Reagents for Organic Synthesis," Vol. 2, Wiley-Interscience, New York, N. Y., 1969, p 171; (b) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

(9) A. P. Krapcho, D. R. Rao, M. P. Silvon, and B. Abegaz, *J. Org. Chem.*, **36**, 3885 (1971).

(10) (a) D. B. Denney and M. J. Boskin, *J. Amer. Chem. Soc.*, **82**, 4736 (1960); (b) R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958).

(11) D. P. G. Hamon, *J. Amer. Chem. Soc.*, **90**, 4513 (1968).

Tetraspiro Compounds.—Treatment of **4** ($n = 6$) with the Simmons-Smith reagent prepared according to the procedure of Shank and Shechter¹² led to tetraspiro **5** ($n = 6$) in 90% yield. The dienes **4** ($n = 5$) and **7** appeared to react much more slowly with the couple prepared by the above procedure and the method recently suggested by Rawson and Harrison¹³ was utilized. Treatment of **4** ($n = 5$) for 36 hr led to a mixture of **5** ($n = 5$) (57%), the trispiro compound **15** ($n = 5$) (26%), and starting diene **4** ($n = 5$) (18%).



These percentages were readily obtained by nmr integrations of the areas in the spectrum of the reaction product. Pure **5** ($n = 5$) was obtained in a 26% yield by vpc collection, and a pure sample of **15** ($n = 5$) was also collected. Treatment of **7** in a similar fashion (48 hr) led to **16** (67%) and **17** (33%). Pure **16** (24% yield) and **17** were obtained by vpc collection. The nmr spectral data for the tri- and tetraspiro compounds along with **16** and **17** are tabulated in Table I for comparative purposes.

TABLE I
NMR DATA FOR THE TRISPIRO AND TETRASPIRO SYSTEMS

Compd ^a	δ , Cyclopropyl -CH ₂ -		δ , =CH ₂	δ , Cycloalkyl-CH ₂ - or CH ₃ -
5 ($n = 5$)	0.37 (s)			1.37 (m)
5 ($n = 6$)	0.50 (s)			1.30 (broad s)
15 ($n = 5$)	0.37 (s)	4.67 (s)		1.60 (m)
16	0.38 (s)			0.77 (s)
17	0.38 (s)	4.75 (s)		1.00 (s)

^a CCl₄ as solvent.

It is of interest to note the chemical shift for the methyl resonances in **7**, monospirene **17**, and dispiro **16**. The $\Delta\delta$ of the methyl resonances in **7** (δ 1.24) and **17** is 0.24 ppm, while the $\Delta\delta$ of the methyl resonances in **17** and **16** is 0.23 ppm. The effect of adding the second cyclopropane ring shows nearly the same upfield shift as the first. Similarly, the ring methylenes for the five-membered ring of **4** ($n = 5$) (δ 1.77, m) shift to 1.60 (m) in **15** ($n = 5$), $\Delta\delta$ 0.17, while the change from **15** ($n = 5$) to **5** ($n = 5$) shows $\Delta\delta$ of 0.23. The anisotropic shielding effect exhibited by the cyclopropanes rings can be rationalized by the ring-current model¹⁴ or on the basis of the bond anisotropy exhibited by the carbon-carbon bonds of the ring.¹⁵

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 237B grating spectrophotometer. Nmr spectra were obtained on a Varian Associates A-60 spectrophotometer, and the peak posi-

(12) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(13) R. J. Rawson and I. T. Harrison, *ibid.*, **35**, 2057 (1970).

(14) (a) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963); (b) J. J. Burke and P. C. Lauterbur, *ibid.*, **86**, 1870 (1964).

(15) K. Tori and K. Kitahonoki, *ibid.*, **87**, 386 (1965), and references cited therein.

tions are reported as parts per million values relative to internal TMS. Gas chromatographic separations were performed on an Aerograph Model A-90-P instrument. Microanalyses were done by Robertson Laboratory, Florham Park, N. J.

Ylide Reactions. Preparation of 4 ($n = 6$). **Procedure A.**—To a stirred suspension of methyltriphenylphosphonium bromide (11.1 g, 0.031 mol) in 80 ml of dry benzene was added under a nitrogen atmosphere, *via* a syringe, 13 ml of a 2.37 *M* *n*-butyllithium solution in hexane (0.030 mol) over a period of 5 min. After the evolution of butane ceased (5 min), a solution of the dione **3** ($n = 6$) (3.0 g, 0.014 mol) in 40 ml of benzene was added dropwise over a period of 10 min. A precipitate appeared and the mixture was heated at reflux for 20 hr. The mixture was cooled and then filtered. The benzene was removed by distillation and the remaining viscous residue was washed repeatedly with pentane. The pentane extracts were chromatographed on 25.0 g of alumina (Camag, Brockmann Number 1) to yield 0.55 g (18%) of **4** ($n = 6$): mp 57–58°; nmr (CCl₄) δ 1.50 (broad singlet, 20 H, ring -CH₂-) and 4.85 ppm (sharp singlet, 4 H, =CH₂); ir (CCl₄) 1640 (m, -C=CH₂ stretch) and 870 cm⁻¹ (s, -C=CH₂ bending).

The analytical sample was crystallized from methanol-pentane, mp 57–57.5°.

Anal. Calcd for C₁₆H₂₄: C, 88.82; H, 11.18. Found: C, 89.01; H, 11.01.

Procedure B.—To a suspension of potassium *tert*-butoxide (5.6 g, 0.05 mol) and *tert*-butyl alcohol (3.7 g, 0.05 mol) in 160 ml of dry benzene methyltriphenylphosphonium bromide (17.9 g, 0.05 mol) was added under a nitrogen atmosphere. The dione **3** ($n = 6$) (4.4 g, 0.02 mol) was added to the yellow mixture and the mixture was refluxed for 20 hr. After cooling in an ice bath the mixture was filtered. The benzene was distilled until 100 ml was collected and the mother liquor was cooled and filtered. The syrupy benzene solution was added to an alumina column and then eluted with pentane. Four 250-ml fractions were collected and fraction 2 on concentration yielded 0.65 g (15%) of **4** ($n = 6$), mp 54–56°.

Preparation of 8.—Sodium hydride (1.2 g, 52 mmol as a 58.6% dispersion in mineral oil) was washed five times with pentane to remove the oil.¹⁶ The reaction was kept under a nitrogen blanket and 20 ml of dry dimethyl sulfoxide was introduced *via* a syringe. The mixture was warmed to 75–80° and stirred for 30 min. The solution was cooled in an ice-water bath and methyltriphenylphosphonium bromide (18.5 g, 52 mmol) dissolved in 50 ml of DMSO was added dropwise. The mixture was stirred at room temperature for 10 min and **6** (3.0 g, 26 mmol) in 40 ml of DMSO was added. The reaction mixture was warmed to 65° and stirred at this temperature for 16 hr. The DMSO was then removed under vacuum and 100 ml of ice-water was added. The residual solid was filtered and dried under vacuum to yield 6.9 g (77%) of **8**. The sample was crystallized from ligroin-benzene to give 5.1 g, mp 138–139° (lit.^{7a} mp 136–137°).

Preparation of 9 ($n = 5$).—The reaction was run as above. From **3** ($n = 5$) (2.0 g, 10 mmol) there was obtained 3.6 g (75%) of **9** ($n = 5$). The sample was crystallized from ligroin-benzene to yield 2.1 g: mp 140–141°; nmr (CDCl₃) δ 1.65 (broad m, 12 H), 2.1 (broad m, 4 H), (ring -CH₂-), 3.05 (m, 1 H, O=CCH), 3.6 (d, 1 H, $J = 25$ Hz, -O=C=CHPPH₃⁺), and 7.5 ppm (m, 15 H, aromatic protons).

Anal. Calcd for C₃₁H₃₃PO₂: C, 79.45; H, 7.09. Found: C, 79.73; H, 7.37.

Preparation of 9 ($n = 6$).—A solution of triphenylphosphine-methylene was prepared under a nitrogen atmosphere from methyltriphenylphosphonium bromide (1.6 g, 4.6 mmol) in 25 ml of dry benzene and 2.0 ml of 2.37 *M* *n*-butyllithium in hexane (4.6 mmol). The dione **3** ($n = 6$) (1.0 g, 4.6 mmol) in 20 ml of benzene was added *via* a syringe. The yellow mixture was refluxed for 15 hr and cooled. The benzene was washed twice with cold water and dried over anhydrous sodium sulfate. The benzene was concentrated by distillation and the residual material was crystallized. On addition of pentane followed by filtration 1.5 g of crude **9** ($n = 6$) (65%), mp 140–155°, was obtained. On solution in ligroin (60–90°) followed by filtration 1.3 g of **9** ($n = 6$) was obtained: mp 161–162°; nmr (CDCl₃) δ 7.6 (complex m, 15 H, aromatic protons), 3.78 (d, 1 H, $J = 25$ Hz, H adjacent to phosphorus), 2.90 (complex

(16) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).

m, 1 H, H adjacent to carbonyl), 1.95 and 1.45 ppm (broad multiplets, 20 H, ring $-\text{CH}_2-$).

Anal. Calcd for $\text{C}_{33}\text{H}_{37}\text{PO}_2$: C, 79.71; H, 7.51. Found: C, 79.74; H, 7.31.

Reaction of Dimethylsulfoxonium Methylide with 6. Preparation of 12.—A solution of the ylide was prepared under nitrogen from trimethylsulfoxonium iodide (9.2 g, 42 mmol), sodium hydride (2.2 g of a 58.6% dispersion in mineral oil, 42 mmol) and 50 ml of dry DMSO.⁸ A solution of 6 (2.8 g, 20 mmol) in 40 ml of DMSO was added with stirring *via* a syringe. The mixture was stirred at room temperature for 2 hr and then heated to 50–55° for 1 hr. The mixture was poured into cold water (250 ml) and extracted with two 150-ml portions of methylene chloride. After drying the extracts over potassium carbonate, the solvent was removed on a rotary evaporator. The residue was further concentrated under vacuum pump pressure. The crude product was treated with ether to yield a crystalline solid, 1.7 g (37%), mp 63–65°. The solid was crystallized from pentane–benzene: mp 64–65°; nmr (CDCl_3) δ 4.52 (s, 1 H, $\text{OS}^+\text{C}-\text{H}-$), 3.41 [s, 6 H, $(\text{CH}_3)_3\text{S}^+\text{O}$], 3.0 (septet, 1 H, $-\text{CH}-$), 1.30 [s, 6 H, $\text{O}=\text{CC}(\text{CH}_3)_2\text{C}=\text{O}$], and 1.05 ppm [d, 6 H, $(\text{CH}_3)_2\text{CH}-$]; ir (CCl_4) 1705 ($-\text{C}=\text{O}$) and 1550 cm^{-1} ($-\text{CH}=\text{C}^--\text{O}$).

Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_3\text{S}$: C, 56.86; H, 8.68; S, 13.82. Found: C, 57.17; H, 9.00; S, 14.11.

Diepisulfide Desulfurizations. Preparation of 7.—The mixture of *cis*- and *trans*-13 (0.9 g, 4.5 mmol) and tri-*n*-butylphosphine (3.0 g, 15 mmol) was heated with stirring in an oil bath at 80° for 60 hr under a nitrogen atmosphere. The diene 7 sublimed and collected in the lower part of the condenser. The solid was removed from the condenser and purified by sublimation at atmospheric pressure and room temperature: yield 0.41 g (67%); mp 65–66° (lit.¹¹ mp 66–68°); nmr (CDCl_3) δ 1.24 (s, 12 H, CH_3-) and 4.75 ppm (s, 4 H, $=\text{CH}_2$).

Preparation of 4 ($n = 5$).—*cis*- and *trans*-14 ($n = 5$) (1.2 g, 4.8 mmol) and tri-*n*-butylphosphine (2.0 g, 10 mmol) were heated with stirring at 100° for 36 hr in a nitrogen atmosphere. The reaction mixture was chromatographed on alumina (100 g, neutral) using pentane to yield 0.70 g (73%) of 4 ($n = 5$). The diene was purified by distillation: bp 45–50° (0.1 mm); nmr (CDCl_3) δ 1.77 (broad peak, 16 H, cyclopentyl $-\text{CH}_2-$) and 4.78 ppm (s, 4 H, $=\text{CH}_2$); ir (CCl_4) 1640 (m, $-\text{C}=\text{CH}_2$ stretch) and 875 cm^{-1} (s, $-\text{C}=\text{CH}_2$ bending).

Anal. Calcd for $\text{C}_{14}\text{H}_{20}$: C, 89.40; H, 10.60. Found: C, 89.10; H, 10.80.

Preparation of 4 ($n = 6$).—The diepisulfides 14 ($n = 6$) (0.4 g, 1.4 mmol) and tri-*n*-butylphosphine (1.4 g, 7 mmol) were heated with stirring at 100° for 18 hr in a nitrogen atmosphere. The residue was chromatographed on neutral alumina with pentane to yield 0.21 g (70%) of 4 ($n = 6$), mp 55–56°. This product was identical in all respects with the compound obtained by the Wittig procedure.

Simmons–Smith Reaction. Preparation of 16 and 17.—Zinc dust (8.5 g, 0.13 mol) and cuprous chloride (1.3 g, 0.13 mol) in 40 ml of anhydrous ether were refluxed with stirring for 30 min under a nitrogen atmosphere.¹³ Methylene iodide (5.2 ml, 0.065 mol) was added and the mixture was refluxed for 30 min. The diene 7 (0.7 g, 0.005 mol) in 5 ml of ether was added and the mixture was refluxed for 48 hr. The ether was removed by decantation, washed with two 10-ml portions of a 5% ammonium chloride solution and two 10-ml portions of a saturated sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. Removal of the ether under water aspirator pressure yielded 0.5 g of crude product: nmr (CCl_4) δ 0.38 (s), 0.77 (s), 1.00 (s), and 4.75 (s). From the peak areas one can calculate

the composition of the crude product to be 33% of monocyclopropane 17 and 67% of dispirocyclopropane 16. Pure 16 was obtained by vpc collection on a 6-ft column of 20% silicone oil on firebrick at 80°: yield 0.18 g (24%); mp 134–135°; nmr (CCl_4) δ 0.38 (s, 8 H, cyclopropane $-\text{CH}_2-$) and 0.77 ppm (s, 12 H, CH_3-).

Anal. Calcd for $\text{C}_{12}\text{H}_{20}$: C, 87.73; H, 12.27. Found: C, 87.57; H, 12.47.

A reasonably pure sample of the monocyclopropane 17 (mp 108–109°) was collected from the vpc column: nmr (CCl_4) δ 0.38 (s, 4 H, cyclopropane $-\text{CH}_2-$), 1.00 (s, 12 H, CH_3-), and 4.75 ppm (s, 2 H, $-\text{CH}_2$).

Preparation of 5 ($n = 5$) and 15 ($n = 5$).—The above procedure was followed for the preparation of the Simmons–Smith reagent. Compound 4 ($n = 5$) (0.35 g, 1.8 mmol) in 5 ml of ether was added to the reagent and the mixture was refluxed for 36 hr. The ether was removed by decantation and washed as above. On removal of the ether the crude mixture which was obtained consisted of 5 ($n = 5$) (57%), the monocyclopropane 15 ($n = 5$) (26%), and starting material (18%). Pure 5 ($n = 5$) was obtained by vpc separation on a 6-ft column of 20% silicone oil on firebrick at 150°: yield 0.1 g (28%); mp 34–34.5°; nmr (CCl_4) δ 0.37 (s, 8 H, cyclopropane $-\text{CH}_2-$), and 1.37 ppm (m, 16 H, cyclopentane $-\text{CH}_2-$).

Anal. Calcd for $\text{C}_{16}\text{H}_{24}$: C, 88.90; H, 11.10. Found: C, 88.94; H, 11.29.

A sample of the monocyclopropane 15 ($n = 5$) was also collected from the vpc column: nmr (CCl_4) δ 0.37 (s, 4 H, cyclopropane $-\text{CH}_2-$), 1.60 (m, 16 H, cyclopentyl $-\text{CH}_2-$), and 4.67 ppm (s, 2 H, $=\text{CH}_2$).

Anal. Calcd for $\text{C}_{15}\text{H}_{22}$: C, 89.04; H, 10.96. Found: C, 89.37; H, 10.98.

Preparation of 5 ($n = 6$).—The zinc–copper couple was prepared from zinc (0.68 g, 10 g-atoms) following the procedure of Shank and Shechter.¹² Methylene iodide (2.06 g, 7.4 mmol) in 50 ml of ether was added to the couple and the mixture was refluxed for 30 min. A solution of 4 ($n = 6$) was added to the reagent. The mixture was refluxed for 18 hr and then filtered. The ethereal filtrate was washed with two 5-ml portions of saturated ammonium chloride, two 5-ml portions of 5% sodium bicarbonate, and two 5-ml portions of water. After drying over anhydrous magnesium sulfate the ether was removed to yield 0.40 g (90%) of crude 5 ($n = 6$). On solution in pentane and cooling to -25° colorless crystals were obtained: mp 45–46°; nmr (CCl_4) δ 0.50 (s, 8 H, cyclopropane $-\text{CH}_2-$) and 1.30 ppm (s, 20 H, cyclohexane $-\text{CH}_2-$); ir (CCl_4) 2050 (s) and 905 cm^{-1} (m).

The analytical sample was crystallized from ethanol, mp 45–46°.

Anal. Calcd for $\text{C}_{18}\text{H}_{28}$: C, 88.45; H, 11.55. Found: C, 88.40; H, 11.60.

Registry No.—4 ($n = 5$), 34202-02-3; 4 ($n = 6$), 34220-26-3; 5 ($n = 5$), 34226-15-8; 5 ($n = 6$), 25517-28-6; 9 ($n = 5$), 34219-90-4; 9 ($n = 6$), 34219-91-5; 12, 34219-92-6; 15 ($n = 5$), 34202-04-5; 16, 34219-93-7; 17, 34219-94-8.

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