Pmr analysis showed that the 6:8 ratio in this experiment was 9:1.

cis,anti,cis-6-Methyltricyclo[5.3.0.0^{2,6}]decan-3-one (6) and *cis,syn,cis*-6-Methyltricyclo[5.3.0.0^{2,6}]decan-3-one (7).—These tricyclic ketones, needed for comparison with the photoproducts, were prepared as previously outlined.[4]

1-Methyltricyclo[4.4.0.0^{2,7}]decan-8-one (8).—This tricyclic ketone was prepared as previously outlined.[18]

(18) C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Amer. Chem. Soc.*, **89**, 4133 (1967).

Registry No.—**5**, 32721-52-1; **11**, 21531-35-1; **12**, 21531-36-2; **13**, 21531-37-3; **14**, 21531-38-4; **15**, 21531-39-5; **16**, 21531-40-8; **17**, 32721-51-0; **18**, 32721-48-5; **19**, 32721-49-6; **20**, 32721-50-9; **26**, 32721-53-2.

Acknowledgments.—We gratefully acknowledge financial support by the National Science Foundation and the Public Health Service.

Stereochemistry of Alkaline Cleavage of Some Phospholanium Salts[1]

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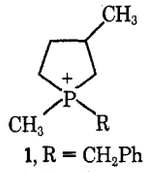
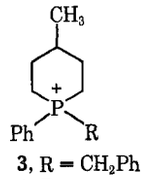
The geometric isomers of 1-benzyl-3-methyl-1-phenylphospholanium bromide (**5a** and **5b**) undergo hydroxide cleavage of benzyl which is accompanied by complete retention of configuration at phosphorus yielding pure isomers of 3-methyl-1-phenylphospholane 1-oxide (**6a** or **6b**). Cleavage of either isomer of 1,3-dimethyl-1-phenylphospholanium bromide (**7a** and **7b**) produces identical mixtures of cis and trans isomers of 1,3-dimethylphospholane 1-oxide (**2**). Base decomposition of the 3-methyl-1,1-diphenylphospholanium salt **8** yields a mixture of about equal parts of **6a** and **6b**.

The cis or the trans phosphonium salt of **1** will undergo cleavage with aqueous sodium hydroxide to afford the corresponding oxide **2** with complete retention of configuration at phosphorus.[2] Recently it was shown that the cis and trans isomers of 1-benzyl-4-methyl-1-phenylphosphorinanium bromide (**3**) are decomposed under the same conditions into nonidentical mixtures of the isomeric phosphine oxides (**4**).[3] For the latter study, the 1-phenyl rather than the 1-methyl compounds were chosen because of synthetic convenience.[4] Since Trippett, *et al.*,[5] report that the base cleavage results of *cis*-1-benzyl-1-phenyl-2,2,3,4,4-pentamethylphosphetanium bromide (**11**) are different from those of the trans isomer where the two compounds differ *configurationally*, we were cautioned against the assumption that the *substitutionally* different 1-methyl-1-benzyl- and 1-phenyl-1-benzylphospholanium salts (**1** and **5**, respectively) would behave identically. We were therefore prompted to investigate the stereochemistry of cleavage of the cis and trans isomers of **5** in order to determine conclusively that the dissimilarity in stereochemical behavior between **1** and **3** is indeed due to ring size and *not* differences in substitution at phosphorus.

The stereochemistry of base cleavage of the geometrical isomers of **7** was also investigated to enable a more confident correlation to be made between leaving group ability and stereochemistry of cleavage. Of the two stereochemical studies reported in the phospholane series, benzyl[2] and trichlorosiloxide[6] as leaving groups give, respectively, retention and inversion of configuration. We have now found that phenyl as a leaving group from *cis*- or *trans*-**7** provides identical mixtures of oxides. Since phosphine oxides are known to be configurationally stable toward aqueous sodium hydroxide,[2,3,6,7] it is plausible to assume that *cis*- and *trans*-**7** lead to a common intermediate preceding phosphine oxide (**2**) formation. In fact, we have found that, when either *cis*-**7** or *trans*-**7** are separately treated with 0.5 equiv of sodium hydroxide under cleavage conditions, the remaining undecomposed salt can be shown to consist of an approximate 1:1 mixture of cis and trans salts. Treatment of either *cis*- or *trans*-**7** with a trace of base at room temperature, however, was insufficient to produce stereomutation at phosphorus to a detectible extent.



1, R = CH_2Ph
2, R = O^-



3, R = CH_2Ph
4, R = O^-

Scheme I summarizes the stereochemical outcome of cleavage reactions of the five pure *P*-phenylphospholanium salts covered by this study.

The retention of configuration at phosphorus for **1** and **5** may be accounted for by (a) equatorial loss of benzyl *via* the conjugate base[8] of the initially formed phosphorane (**9**),[2] and/or (b) apical loss of benzyl from the conjugate base of **10** after an incomplete pseudorotational process.[9] If formed, **10** would be expected to lose benzyl *via* its conjugate base.[8] Placement of oxygen in the equatorial position of **10** can be

(1) This investigation was supported by National Science Foundation Grants No. GP-7407 and GP-25479. A preliminary account of a portion of this work is found in ref 6.

(2) (a) K. L. Marsi, *Chem. Commun.*, 846 (1968); (b) *J. Amer. Chem. Soc.*, **91**, 4724 (1969).

(3) K. L. Marsi and R. T. Clark, *J. Amer. Chem. Soc.*, **92**, 3791 (1970).

(4) G. Maerkl, *Angew. Chem., Int. Ed. Engl.*, **2**, 620 (1963).

(5) J. R. Corfield, J. R. Shutt, and S. Trippett, *Chem. Commun.*, 789 (1969). The *cis*- and *trans*-1-benzyl-1-methyl-2,2,3,4,4-pentamethylphosphetanium bromides are also reported to give nonidentical products on base cleavage. However, it should be noted that the results of this work are at variance with the work of Cremer, *et al.* (ref 12), on the same systems and under similar conditions.

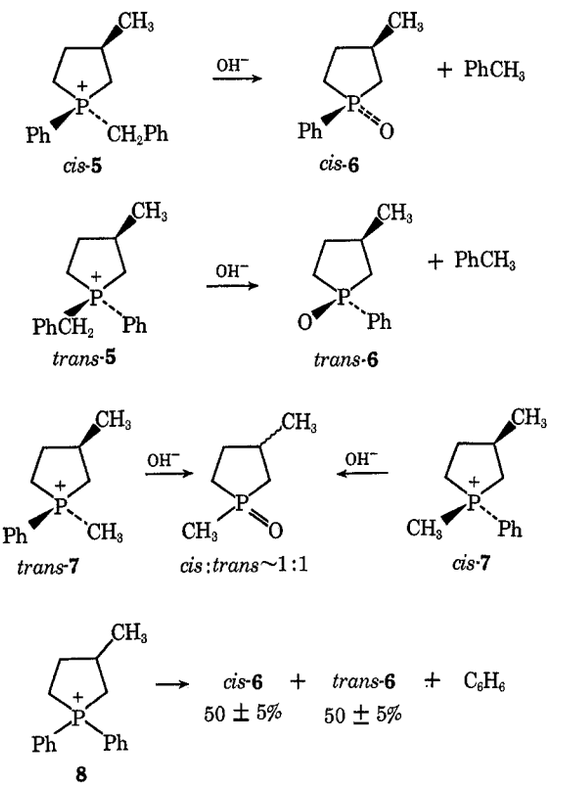
(6) W. Egan, G. Chauviere, K. Mislow, R. T. Clark, and K. L. Marsi, *Chem. Commun.*, 733 (1970).

(7) K. F. Kumli, W. E. McEwen, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **81**, 3805 (1959). These references give a representative, but not exhaustive, list of such examples.

(8) W. E. McEwen in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1965, Chapter 1.

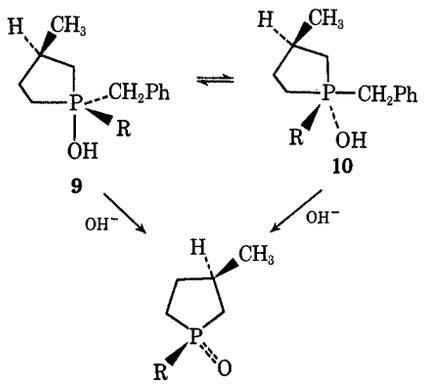
(9) K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970).

SCHEME I[a]



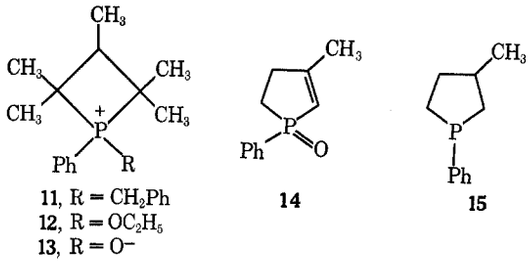
[a] Prefixes cis and trans relate the stereochemistry of the C-methyl and the P substituent surviving the cleavage reaction.

defended since it is the less electronegative oxide oxygen which occupies that position in the reactive intermediate.[10]



The phosphonium salts **1** and **5** evidently represent examples for which the energy barrier between the initially formed phosphorane (**9**) and one or more pseudorotational transformations leading to an equilibrium mixture of phosphoranes (and hence to a mixture of diastereomeric oxides) is higher than stereospecific loss of a benzyl group by mechanism a and/or b above. However, in the case of alkaline cleavage of either the cis or trans isomer of **7** the reaction energetics are apparently reversed. For the cleavage of **7** the attainment of equilibrium among pseudorotational forms of the phosphorane intermediate leading to identical mixtures of both isomers of **2** must occur more rapidly than stereospecific loss of phenyl. This is a reasonable explanation since benzyl is known to be a superior leaving group to phenyl.[11]

Similar observations have been made by others in the phosphetanium series. For example, either the cis or trans isomer of **11** is reported to give identical mixtures of phosphetane 1-oxides (**13**)[12] when treated with aqueous sodium hydroxide, whereas cleavage of the analogous ethoxy isomers (**12**) occurs stereospecifically with retention of configuration at phosphorus.[13] A rigorous explanation of these phenomena has been advanced by Mislow.[9,13]



The outcome of the cleavage of **8** may be explained in the same manner as for **7**, although, of course, the mixture of oxides could be accounted for without invoking pseudorotation since the phosphorus atom of **8** is achiral. If the latter is true, which seems unlikely in view of the cleavage results of **7**, the methyl group exerts no perceptible steric effect on the stereochemistry of cleavage of **8**.

Synthetic Procedures.—The ring system of **5** and **7** was constructed by the McCormack cycloaddition reaction[14] of isoprene with phenyldichlorophosphine. After hydrolysis of the adduct, the resulting 3-methyl-1-phenyl-2-phospholene 1-oxide (**14**)[15] was hydrogenated in the presence of a palladium-on-carbon catalyst, the reduction occurring completely stereospecifically within the limits of pmr detection (about ±5%) to give an oxide (**6a**), mp 60–61°, bp 115–125° (0.05 mm). This oxide was reduced with phenylsilane, a conversion known to occur stereospecifically with retention of configuration.[2b] The phosphine (**15a**) thus obtained was quaternized with benzyl bromide or methyl bromide to yield the corresponding phosphonium salts **5a**, mp 171.5–172°, or **7a**, mp *ca.* 100°, a reaction known to proceed with retention of configuration at phosphorus.[16] Cleavage of **5a** with refluxing 1 *N* NaOH yielded **6a** having the same characteristics as the oxide obtained by hydrogenation of **14**. The diastereomeric phosphonium salts **5b**, mp 179.5–180°, and **7b**, mp 158.5–159°, were obtained by treatment of the oxide **6a** with hexachlorodisilane[6,17] followed by careful fractional distillation on a spinning band column of the resulting mixture of diastereomeric phosphines and quaternization of the final fraction with benzyl bromide or methyl bromide.

(10) B. R. Ezzell, *J. Org. Chem.*, **35**, 2426 (1970).

(11) J. Meisenheimer and L. Lichtenstadt, *Ber.*, **44**, 356 (1911); G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

(12) S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *Chem. Commun.*, 769 (1969).

(13) K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7027 (1969).

(14) W. B. McCormack, U. S. Patents 2,663,736 and 2,663,737 (Dec 22, 1953); L. D. Quin in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, Chapter 3.

(15) L. D. Quin and T. P. Barket, *Chem. Commun.*, 914 (1967); L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, **33**, 1034 (1968).

(16) L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, **92**, 4303 (1970).

(17) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7012 (1969).

Retention of configuration for the base cleavage of the pure salts **5a** and **5b** was established by reduction with phenylsilane of the oxides resulting from cleavage of these salts, quaternizing the resulting phosphine with benzyl bromide, and demonstrating by pmr and mixture melting points the identity of the salts thus obtained with samples of the salts submitted to cleavage. Mixtures of oxides **2a** and **2b** ensuing from the cleavage of pure **7a** and **7b** were analyzed by pmr with advantage being taken of the differences in chemical shifts of the benzyl protons of the diastereomeric salts obtained from benzylation of the phosphine mixtures yielded by phenylsilane reduction of the oxide mixtures. The mixture of oxides **6a** and **6b**, derived from the base decomposition of pure **8**, was similarly analyzed.

Compound **8** was prepared as an eventual alternate route to **15b**, but hexachlorodisilane reduction of **6a** was found to provide a more straightforward access to this compound. The preparation of **8** was accomplished by an adaptation of the Maerkl procedure.[4] The bromide salt of **8** proved to be an intractable oil; therefore, the crystalline hexafluorophosphate[18] salt was prepared, purified, and cleaved.

Experimental Section

General.—Melting points were determined on a Thomas–Hoover 6406-K melting point apparatus in capillary tubes (sealed with silicone grease for hygroscopic materials) and are uncorrected; boiling points are also uncorrected. ^{1}H nmr spectra were measured at 60 MHz with a Jeolco C-60H spectrometer. Operations involving trivalent phosphorus compounds were conducted in a nitrogen atmosphere. Moisture-reactive halophosphines and very hygroscopic phosphine oxides were handled in a dry atmosphere. Solvents used were dried and/or distilled prior to use. Stereoisomeric compounds used were estimated to be more than 95% isomerically pure as evidenced by nmr analysis.

3-Methyl-1-phenyl-2-phospholene 1-Oxide (14).—This compound was prepared according to the procedure given in ref 15.

3-Methyl-1-phenylphospholane 1-Oxide (6a).—To 121.5 g (0.633 mol) of **14** in 150 ml of absolute ethanol was added 5 g of 5% palladium on carbon, the mixture was hydrogenated in a Paar hydrogenator for 20 hr at 45–49 lb in.$^{-2}$, the solution was filtered, the solvent was removed, and the residue was distilled *in vacuo* to yield 122.5 g of a viscous oil, bp 115–125° (0.05 mm), which upon standing formed a crystalline, hygroscopic solid: mp 60–61°; nmr (CCl_4, TMS) δ 1.1 (d, J = 6 Hz, CCH_3), 1.23–2.67 (m, ring protons), 7.23–8.1 (m, PC_6H_5).

Anal. Calcd for $C_{11}H_{15}PO$: C, 68.02; H, 7.79. Found: C, 68.10; H, 8.04.

3-Methyl-1-phenylphospholane (15a).—To 8.0 g (0.041 mol) of **6a** in a 25-ml flask cooled to 0°, 4.43 g (0.041 mol) of phenylsilane was added *via* pipet in a nitrogen atmosphere. The reaction mixture was warmed to 60°. Upon cessation of effervescence, the phosphine was distilled to yield 6.75 g of **15a**: bp 49–51° (0.01 mm); nmr (CCl_4, TMS) δ 1.1 (d, J = 6 Hz, CCH_3), 1.23–2.67 (m, ring protons), 7.23–8.1 (m, PC_6H_5).

1-Benzyl-3-methyl-1-phenylphospholanium Bromide (5a).—To 3.1 g (0.0174 mol) of pure **15a** in 10 ml of benzene, 6 g (0.0350 mol) of benzyl bromide dissolved in 10 ml of benzene was added dropwise with stirring. White crystals began separating almost immediately. The mixture was refrigerated overnight and yielded 6.5 g of crude **5a**, mp 169–169.8°. Recrystallization from 1:15 EtOH–EtOAc produced 5.15 g of pure **5a**: mp 171.5–172°; nmr (D_2O, DSS) δ 1.1 (d, J = 5.3 Hz, CCH_3), 1.4–3.2 (m, ring protons), 3.95 (d, J = 15 Hz, PCH_2Ph), 6.9–7.4 (m, PC_6H_5), 7.4–7.9 (m, PCC_6H_5).

Anal. Calcd for $C_{18}H_{22}BrP$: C, 54.37; H, 7.02. Found: C, 54.29; H, 7.24.

Reaction of 5a with Sodium Hydroxide.—To a 25-ml flask containing 2.0 g (0.0057 mol) of **5a** was added 11.5 ml of 1 N sodium hydroxide. The resulting solution was refluxed gently for 20 hr. Early formation of an organic layer indicated that the reaction was probably complete within the first 2 hr. Vpc analysis of the organic layer removed by azeotropic distillation showed only toluene. The aqueous residue was saturated with potassium hydroxide and extracted with chloroform. The chloroform solution was concentrated and the residue was distilled at bp 120° (0.01 mm), yielding 0.8 g of liquid **6a**: nmr (CCl_4, TMS) δ 1.1 (d, J = 6 Hz, CCH_3), 1.23–2.67 (m, ring protons), 7.23–8.1 (m, PC_6H_5). **6a** was reduced with phenylsilane as described above and the distillate, **15a**, bp 62–68° (0.02 mm), quaternized with benzyl bromide to give crystals identical with **5a** in melting point and nmr.

3-Methyl-1-phenylphospholane (15b).—To 26.4 g (0.136 mol) of **6a** in 100 ml of benzene was added dropwise with stirring at room temperature 47.5 g (0.176 mol) of hexachlorodisilane in 50 ml of benzene.[6] Upon completion of the addition, the resulting solution was refluxed for an additional 0.5 hr and cooled to 0° and 100 ml of 30% sodium hydroxide was added dropwise with stirring over a period of 2 hr. A precipitate of white polymeric material separated during this addition. The liquid phase was decanted in a glove bag under nitrogen, the precipitate was washed several times with benzene, and the benzene extracts were combined. After drying over anhydrous sodium sulfate, benzene was removed and the residual phosphine was distilled at reduced pressure, providing 14.55 g of a mixture of **15a** and **15b**, bp 84–88° (0.2 mm). Although attempts to achieve vpc separation of the two isomers were not successful, considerable enrichment was accomplished by use of a Nestor-Faust Auto Annular Teflon spinning band column. Five fractions totaling 13.25 g were collected at 51° (0.02 mm) over a period of 14 hr: nmr (neat, TMS), **15a**, δ 0.93 (d, J = 6 Hz); **15b**, δ 0.81 (d, J = 6 Hz). Nmr showed that the last three fractions, totaling 6.2 g, were very highly enriched in **15b**.

1-Benzyl-3-methyl-1-phenylphospholanium Bromide (5b).—**15b** (3.53 g), obtained as the last fraction of the preceding experiment, was quaternized in benzene with benzyl bromide in a glove bag under dry nitrogen. Crystals formed immediately and were allowed to stand overnight. The crude crystals (5.7 g), mp 165.5–167°, were recrystallized four times from EtOH–EtOAc to a constant melting point of 179.5–180°. Nmr analysis of the final product indicated complete absence of **5a**: nmr (D_2O, DSS) δ 1.1 (d, J = 5.3 Hz, CCH_3), 1.4–3.2 (m, ring protons), 3.98 (d, J = 15 Hz, PCH_2Ph), 6.9–7.4 (m, PC_6H_5), 7.4–7.9 (m, PCC_6H_5).

Anal. Calcd for $C_{18}H_{22}PBr$: C, 61.89; H, 6.32. Found: C, 62.17; H, 6.45.

Reaction of 5b with Sodium Hydroxide.—**5b** (1.96 g) was made to react with 1 N sodium hydroxide under the same conditions as described above for **5a**. **6b** (0.52 g), bp 120° (0.01 mm), was obtained: nmr (CCl_4, TMS) δ 1.16 (d, J = 5.3 Hz, CCH_3), 1.4–2.6 (m, ring protons), 7.4–8.3 (m, PC_6H_5). Reduction with phenylsilane gave **15b**, bp 62–68° (0.02 mm), which was quaternized with benzyl bromide to provide a crystalline material identical in melting point and nmr with **5b**.

1,3-Dimethyl-1-phenylphospholanium Bromide (7a).—To 7.6 g (0.082 mol) of methyl bromide dissolved in 25 ml of dry benzene was added dropwise with stirring 3.65 g (0.0206 mol) of **15a** in 10 ml of benzene. The reaction mixture was stored in the refrigerator, and the very hygroscopic crystals subsequently were removed in a glove bag under dry nitrogen, yielding 5.45 g (0.0199 mol) of **7a**. The salt oiled out upon attempted recrystallization from dry ethanol and was finally recrystallized from ethyl acetate. Due to its tenacity for traces of water, a sharp melting point could not be obtained for this compound, mp 100–130° (mainly at 100°). However, the nmr spectrum was completely consistent with an isomerically pure salt: nmr (D_2O, DSS) δ 1.26 (d, J = 4.5 Hz, CCH_3), 2.3 (d, J = 14.3 Hz, PCH_3), 1.5–2.1 (m, ring protons), 7.5–8.1 (m, PC_6H_5).

Anal. Calcd for $C_{12}H_{18}PBr \cdot 0.15H_2O$: C, 52.24; H, 6.69. Found: C, 52.10; H, 6.46.

1,3-Dimethyl-1-phenylphospholanium Bromide (7b).—**15b** (6.2 g, 0.0348 mol), from spinning band fractionation of **15a** and **15b**, was added dropwise to a stirred solution of 13.3 g (0.14 mol) of methyl bromide in 25 ml of benzene; the slightly hygroscopic crystals were filtered in a glove bag, yielding 8.7 g (0.318 mol) of isomerically impure **7b**, mp 155–158°. Seven recrystallizations from 1:5 EtOH–EtOAc yielded pure **7b**, mp 158.5–159°. Nmr analysis verified the absence of **7a**: nmr (D_2O, DSS) δ 1.26

(18) D. B. Denney and S. M. Felton, *J. Amer. Chem. Soc.*, **90**, 183 (1968).

(d, J = 4.5 Hz, CCH_3), 2.3 (d, J = 14.25 Hz, PCH_3), 1.5–2.1 (m, ring protons), 7.5–8.1 (m, PC_6H_5).

Anal. Calcd for $C_{12}H_{18}PBr$: C, 52.76; H, 6.64. Found: C, 52.51; H, 6.85.

Reactions of **7a** and **7b** with sodium hydroxide were carried out as for **5a**. Vpc analysis of the organic layer obtained by azeotropic distillation of the reaction mixture showed only benzene to be present. Distillation of the oxide mixture derived from 2.0 g of **7a** or **7b** gave 0.40 and 0.45 g, respectively, both of bp 70–80° (0.1 mm) and mp 45–57°. The nmr spectra were identical in every respect: nmr (CCl_4, TMS) δ 1.07 (d, J = 6 Hz, CCH_3), 1.13 (d, J = 5.3 Hz, CCH_3), 1.5 (d, J = 12.5 Hz, PCH_3), 1.3–2.6 (m, ring protons). The two oxide mixtures were separately reduced with phenylsilane and quaternized with benzyl bromide, each giving a phosphonium salt mixture of mp 154–164°. Comparison of the nmr spectra of these mixtures with those of known mixtures prepared from pure cis and trans isomers of 1-benzyl-1,3-dimethylphospholanium bromide[2] showed the unknown mixtures to consist of about equal quantities of the two isomers.

Synthesis of 3-Methyl-1,1-diphenylphospholanium Hexafluorophosphate (8).—A mixture of 50.0 g (0.217 mol) of 1,4-dibromo-2-methylbutane and 40.2 g (0.108 mol) of tetraphenyldiphosphine in 270 ml of *o*-dichlorobenzene was added dropwise to 750 ml of refluxing *o*-dichlorobenzene over a period of 3 hr. The solvent (800 ml) was removed by distillation, the residue was extracted with water, and the water extract was evaporated, leaving 41.7 g of a dark, acidic oil, from which crystals could not be obtained. A 27-g portion of this oil was dissolved in water and titrated to neutrality with 70 ml of 1 N sodium bicarbonate, extracted with ether and then with chloroform. Evaporation of the chloroform extract yielded 16 g of a dark glassy oil of which a 7-g portion was dissolved in water and to which a saturated solution of 4.0 g of potassium hexafluorophosphate was added.[18] The gummy precipitate formed was triturated with ether. Repeated recrystallizations from absolute ethanol gave a compound of mp 135.5–136.5°.

Anal. Calcd for $C_{17}H_{20}P_2F_6$: C, 51.01; H, 5.03. Found: C, 51.08; H, 5.31.

Reaction of 8 with Sodium Hydroxide.—Sodium hydroxide (1N, 12 ml) was added to a 25-ml flask containing 2.0 g (0.006 mol) of **8**. The resulting suspension (the hexafluorophosphate salt is only slightly soluble in H_2O) was refluxed gently for 43 hr. The oxide mixture was worked up as described for the cleavage reaction of **5a** and yielded 0.62 g of a mixture of oxides **6a** and **6b**, bp 120–125° (0.05 mm). Following previously outlined procedures, the oxide mixture was reduced with phenylsilane and quaternized with benzyl bromide to give a 93% yield of salt mixture of mp 150–156°. Comparative nmr analysis using known mixtures of pure **5a** and **5b** showed this to be an approximately equal mixture of the two isomers.

Base-Catalyzed Isomerization of 7a and 7b.—To a 2-ml pear-shaped flask was added 200 mg (733 μmol) of pure **7a**, 15 mg (375 μmol) of sodium hydroxide, and 0.3 ml of water. The reaction mixture was refluxed gently for a period of 16 hr. The ^{31}P nmr spectrum (220 MHz Varian spectrometer) of the reaction mixture provided two peaks of equal area at +95.84 and +96.00 ppm (relative to trimethyl phosphite) as compared with a control solution (100 mg of **7a** in 0.3 ml of water) which showed a single peak at +95.78 ppm.

An identical study was conducted on a mixture of **7a** and **7b** (27% **7a** and 73% **7b**). After base treatment the ^{31}P nmr spectrum showed two signals of equal intensity at +95.94 and +96.09 ppm as compared with the untreated mixture (100 mg salt mixture in 0.3 ml water), which showed signals at +95.86 and +96.01 ppm in the ratio of 27:73, respectively.

Registry No.—*cis*-**5**, 32721-82-7; *trans*-**5**, 32721-83-8; *cis*-**6**, 29587-76-6; *trans*-**6**, 29587-77-7; *cis*-**7**, 32721-23-6; *trans*-**7**, 32721-24-7; **8**, 32721-25-8; *cis*-**15**, 32721-26-9; *trans*-**15**, 32721-27-0.

Acknowledgments.—We wish to express out gratitude to Dr. Frank Lin for determining nmr spectra and to the California Institute of Technology for use of the 220-MHz spectrometer.

Thujopsene Rearrangements. The Ring System *via* Methyl Group Migration[1-3]

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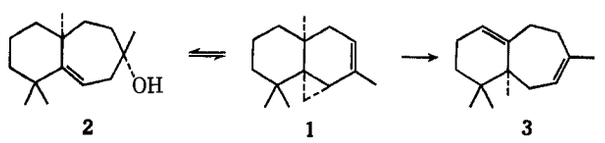
Received July 7, 1971

Under mild acid conditions, *cis*-thujopsene rearranges to 1,4,11,11-tetramethylbicyclo[5.4.0]undeca-3,7-diene (**3**). This diene when treated with 0.02 M perchloric acid in refluxing acetic acid rearranges to tricyclic olefin **4** whose structure was proved by degradation and by partial synthesis. This extensive rearrangement which involves a ring closure and two methyl group migrations finds its thermodynamic driving force in the low free energy of the product. The mechanism of the rearrangement is discussed and its relationship to the rearrangement of caryophyllene to neoclovene is noted.

Part A

Under mild acidic conditions, 0.02 M perchloric acid in aqueous dioxane, the equilibrating cyclopropylcarbinyl and homoallyl cations from *cis*-thujopsene (**1**) and widdrol (**2**), respectively, are irreversibly converted by a ring enlargement and angular methyl group migration to the diene **3**.[2] This diene is the major product formed under these acidic conditions and it is stable for long periods, but it is slowly consumed in another reaction. This latter process has now been evaluated by studying the rearrangement of *cis*-thujopsene under more vigorous reaction conditions, namely, 0.02 M perchloric acid in refluxing acetic acid. Under these conditions the rearrangement proceeded past diene **3** and a completely different set of reaction products was formed. Three hydrocarbons in a ratio of 14:4:3 were obtained and in this paper the structure of the major hydrocarbon and its mechanism of formation will be discussed.



2 **1** **3**

Through a series of degradation and synthetic steps, the structure of the major hydrocarbon was established as the tricyclic olefin **4**. A possible pathway for the rearrangement of *cis*-thujopsene (**1**) to this olefin **4** may conveniently involve the diene **3** as an intermediate.

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(2) For previous papers in this study see (a) W. G. Dauben and L. E. Friedrich, *Tetrahedron Lett.*, 2675 (1964); (b) W. G. Dauben and L. E. Friedrich, *ibid.*, 1735 (1967); (c) W. G. Dauben and E. I. Aoyagi, *Tetrahedron*, **26**, 1249 (1970); (d) W. G. Dauben, L. E. Friedrich, P. Oberhänsli, and E. I. Aoyagi, *J. Org. Chem.*, **37**, 9 (1972).

(3) This work appeared in the Abstracts, IUPAC 5th International Symposium on the Chemistry of Natural Products, F-13, London, July 8–13, 1968, p 296.

(4) National Science Foundation Predoctoral Fellow.