compound proved difficult, the original workers abandoned this synthesis in favor of a path[6] analogous to the one which they used in the synthesis of I.[4] The current availability of 16-dehydro-20-keto steroids appreciably shortens the original synthetic scheme[5] and has thus made its reinvestigation appear attractive.

Bromination of 16-dehydropregnenolone acetate (IV) according to the procedure of Inhoffen[7] resulted in formation of the 5,6-dibromide V. The dibromide was not purified since n.m.r. studies indicated that byproduct formation occurred mainly during crystallization. An excess of N-bromosuccinimide was then employed to effect allylic bromination at the 15-position. Subsequently, the tribromide VI was treated with potassium iodide under the conditions specified by the Swiss workers for the regeneration of the 5,6-double bond from tribromide in the synthesis of II.[4] ·As some spontaneous elimination of the allylic bromide was observed[8] during this process, conditions were modified to effect direct conversion of tribromide to I. The above procedure appreciably shortens the synthesis of 14,16-unsaturated steroids, eliminates the need for preparing and dehydrating cyanohydrins (particularly disagreeable steps both because of the toxicity of the reactants and because of the reversibility of the cyanohydrin formation), and reproducibly affords 3β-acetoxy-20-keto-5,14,16-pregnatriene (I) from 16-dehydropregnenolone acetate in greater than 60% yield.

Experimental[9]

3β-Acetoxy-20-keto-5,14,16-pregnatriene (I).—To a solution of 5.024 g. (0.014 mole) of 3β-acetoxy-20-keto-5,16-pregnadiene in 170 ml. of anhydrous ether was added, with stirring, a solution of 10 g. of anhydrous potassium acetate in 100 ml. of glacial acetic acid. The resulting mixture was thoroughly stirred in an ice bath while 2.25 g. (0.14 mole) of bromine in 50 ml. of acetic acid was added dropwise over a period of 3–3.75 hr. The mixture was stirred in the cold an additional 2 hr. and then at room temperature overnight. The product was partitioned between water and ether. The ether solution was washed twice with water, once with aqueous potassium carbonate solution, and then once with water. The organic phase was dried over magnesium sulfate and filtered; the ether was distilled under reduced pressure. The dibromide, 7.184 g., was obtained as a white foam.

A mixture of 7.104 g. (0.014 mole) of dibromide, 4.84 g. (0.028 mole) of N-bromosuccinimide, 75 ml. of carbon tetrachloride, and 20 mg. of 2,2'-azobisisobutyronitrile was stirred and heated under reflux in a nitrogen atmosphere for 1 hr. After the mixture had cooled to room temperature, it was filtered and the solvent was distilled under reduced pressure. The foam which resulted was mixed with 9.548 g. (0.064 mole) of sodium iodide and 75 ml. of acetone and heated under reflux under a nitrogen atmosphere for 3.5 hr. The acetone was then removed under reduced pressure. The residue was partitioned between chloroform and aqueous sodium thiosulfate solution. The chloroform layer was washed with aqueous sodium thiosulfate solution until it was free from iodine, then dried over magnesium sulfate, filtered, and evaporated to dryness under reduced pressure. The crude product, which was obtained as 4.85 g. of brown solid, was chromatographed over 122 g. of Merck acid-washed alumina.

The column was developed using n-hexane, benzene, and ethyl acetate as eluents. The fractions eluted by benzene and by 10:1 benzene–ethyl acetate contained a total of 3.43 g. of solid which was crystallized from acetone to give 3.25 g. of 3β-acetoxy-20-

keto-5,14,16-pregnatriene as pale yellow rectangular plates: m.p. 158–159°, λ_{max}^{EtOH} 309 mμ (ϵ 10,650). Recrystallization from acetone afforded an analytical sample: m.p. 159–160°; λ_{max}^{EtOH} 309 mμ (ϵ 11,270); $[\alpha]^{24}$D +287°, +284° (c 0.217, 0.315, CHCl$_3$) [lit.[4] m.p. 153–154°, $[\alpha]^{17}$D +369°, λ_{max} (of 3β-hydroxy compound) 307 mμ (log ϵ 4.23)][10]; $\lambda_{max}^{CCl_4}$ 5.76, 6.0 (sh), 6.05, 6.57, and 8.07 μ; n.m.r. (CDCl$_3$) δ_{TMS} 1.16 and 1.20 (singlets, 18- and 19-methyl protons), 2.05 (singlet, acetate protons), 2.35 (singlet, C-21 protons), 5.48 (C-6 proton), 6.05 (C-15 proton), and 7.26 (doublet, J = 2 c.p.s., C-16 proton).

Anal. Calcd. for C$_{23}$H$_{30}$O$_3$: C, 77.93; H, 8.53. Found: C, 78.07; H, 8.38.

(10) The optical rotation and extinction coefficient which we determined are in better agreement with the values reported in the literature for related systems than are the values reported for I in ref. 4. For example, the Swiss workers[6] report a log ϵ of 4.1 for III and, based on the rotation which they report for III, one can calculate, by the method of molecular rotation differences, $[\alpha]$D +262° for I. In addition, a material balance on a Diels-Alder reaction of I indicates purity of 90% for this substance.

The Thermal Isomerization of 1,1-Dicyclopropylbutadiene

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The rearrangement of vinylcyclopropanes to cyclopentenes is now a well-documented reaction.[1-5] However, there is little data on the thermal isomerization of 1-cyclopropyl-1,3-butadiene (1) and its derivatives, a system which might be expected to yield seven-membered rings. Doering has reported, without details, that both the *cis* and *trans* forms of 1 rearrange only to 3-vinylcyclopentene and that no cycloheptadiene is observed.[6] The transitory formation of a seven-membered ring in such a system has, however, been postulated by Vogel to explain the equilibrium at 180° between the antipodes of benzonorcaradiene.[7]

The study of 1 is made difficult by the necessity of separating the *cis* (1a) and *trans* (1b) isomers. Unless the bond between carbons 1 and 2 loses all π character in the transition state so that free rotation can occur, only 1a can exist in a conformation in which the cyclopropyl group and terminal vinyl are suitably placed for formation of a seven-membered ring. The probability of such a favorable conformation occurring is, however, greater in the rearrangement of 1,1-dicyclopropyl-1,3-butadiene (2) where the problem of *cis* and *trans* isomers does not exist. The isomerization of this compound has therefore been investigated.

As in the case of 1,1-dicyclopropylethylene,[5] rearrangement involving one cyclopropyl group of 2 should lead to a new vinylcyclopropane system which could undergo further rearrangement. There are consequently four products which can be predicted.

(6) P. A. Plattner, K. Meier, and H. Heusser, *Helv. Chim. Acta.*, **30**, 905 (1947).

(7) H. H. Inhoffen, F. Blomeyer, and K. Bruckner, *Ber.*, **87**, 593 (1954).

(8) This observation was made by B. S.

(9) Melting points are uncorrected and were determined in open capillary tubes on a Mel-Temp apparatus. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were determined on a Perkin-Elmer Infracord Model 137. N.m.r. spectra were determined on a Varian A-60 spectrometer.

(1) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 4891 (1960).

(2) M. C. Flowers and H. M. Frey, *ibid.*, **83**, 3547 (1961).

(3) W. van E. Doering and J. B. Lambert, *Tetrahedron*, **19**, 1989 (1963).

(4) E. Vogel, *Angew. Chem.*, **72**, 4 (1960).

(5) A. D. Ketley, *Tetrahedron Letters*, **No. 25**, 1687 (1964).

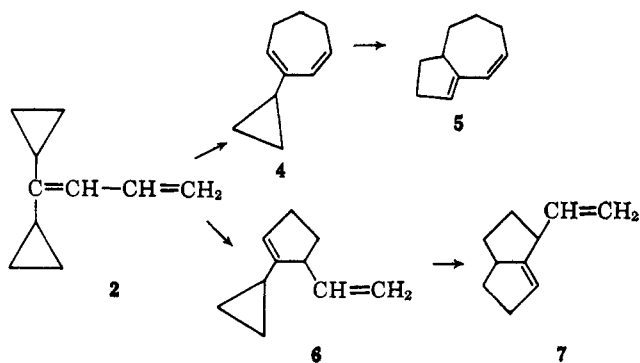(6) W. von E. Doering and W. R. Roth, *Angew. Chem., Intern. Ed. Engl.*, **2**, 115 (1963).

(7) E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

The diene 1,1-dicyclopropylbutadiene was pyrolyzed by passing through a heated Vycor tube packed with glass wool. After one pass through the tube at 400°, 1,1-dicyclopropylbutadiene was completely converted to a mixture containing 85% 1-cyclopropyl-5-vinylcyclopentene and 15% compound 7. No other products were detected. At this temperature 1-cyclopropyl-5-vinylcyclopentene was slowly converted to compound 7, three passes yielding 33% of the latter compound. Compound 7 is believed to be 8-vinylbicyclo[3.3.0]-octene-1 on the basis of its infrared and n.m.r. spectra. The spectra are also consistent with 4-vinylbicyclo-[3.3.0]octene-1 and 6-vinylbicyclo[3.3.0]octene-1. Neither compound, however, is a likely pyrolysis product of 1-cyclopropyl-5-vinylcyclopentene.

The failure to obtain even trace amounts of seven-membered ring compounds from this system was unexpected since examination of Dreiding models of 1,1-dicyclopropylbutadiene suggested that such a rearrangement might occur. However, examination of models approximating the transition state (8), in which it is assumed that carbon 5 has considerable Sp^2 character while the cyclopropyl ring has not completely broken, showed that carbons 1–5 cannot exist in a plane due to interaction between the hydrogens on carbons 4 and 7.
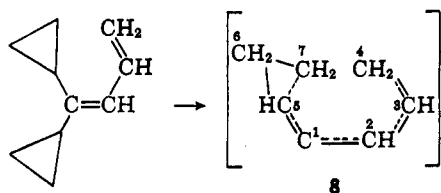
Consequently, a transition state such as 8 is unlikely because the terminal vinyl group cannot enter into resonance with the rest of the system. If, however, we assume that the bond in the cyclopropyl group breaks completely to give a conventional diradical intermediate, steric inhibition of resonance becomes much less likely. Formation of seven-membered rings would then be expected by simple intramolecular coupling of radical ends. That this is not observed provides further evidence for the nonradical character of the vinylcyclopropane rearrangement.

Work currently in progress in this laboratory indicates that vinylcyclopropanes in which the cyclopropyl group is *cis* to an alkyl group rearrange much more slowly than the corresponding *trans* isomers. Hence, it is likely that if the terminal vinyl group of 2 does not interact with the *cis* cyclopropyl group to give a seven-membered ring it will inhibit its rearrangement to the

cyclopentene. The formation of 6 probably involves, therefore, the rearrangement of the cyclopropyl group *trans* to the vinyl group.

Experimental

1,1-Dicyclopropyl-1,3-butadiene (2).—A modification of the method of Begidov, Domareva, and D'yakonov[8] was used to synthesize 2. Dicyclopropylallylcarbinol (20 g.) was mixed with 60 g. of freshly distilled acetic anhydride and heated to 125° for 30 min. Longer heating periods at 125° resulted in extensive polymerization of the product while lower temperatures gave little conversion. Water was then added, the aqueous layer was extracted with ether, and the combined organic material was then washed with 10% sodium carbonate solution. After drying over anhydrous sodium sulfate, the ether was removed and the product was fractionated. A small amount (3.3 g.) of a cut, b.p. 69° (9 mm.), was collected (lit.[8] b.p. of 2 68–70° at 11 mm.) followed by 18.0 g. of unreacted carbinol. The diene prepared in this way always contained some carbinol which could not be fractionated out. Since allylcarbinols decompose to ketones and olefins at relatively low temperatures,[9] the product was passed through a hot tube at 300° for a short period so that the carbinol was converted to dicyclopropyl ketone and propylene but the diene 2 was not rearranged. Pure diene, b.p. 70° (9 mm.), was then isolated from the resulting mixture. The yield was 2.8 g. (14%).

Anal. Calcd. for $C_{10}H_{14}$: C, 89.56; H, 10.54. Found: C, 89.62; H. 10.47.

The infrared spectrum was identical with that of Begidov, *et al.*,[8] except for the absence of bands at 1316, 1240, and 875 cm.$^{-1}$. Since these are present in the spectrum of dicyclopropylallylcarbinol, this material was probably a contaminant in the literature sample. The absence of any absorption in the region 3600–3650 cm.$^{-1}$ established that our sample was free from carbinol. (This region was not included in the literature spectrum.) The n.m.r. spectrum consisted of multiplets at τ 8.90–9.72 (cyclopropyl methylene H, relative area 8) and 7.73–8.31 (cyclopropyl methyne H, relative area 2) and an ABX pattern consisting of a multiplet at τ 4.45 (H at C-4, relative area 2), a doublet at 3.60 (H at C-2, relative area 1), and a multiplet at 2.46 (H at C-3, relative area 1).

1-Cyclopropyl-5-vinylcyclopentene (6).—The diene 2 was passed three times through a Vycor tube 60 cm. long and 2.7 cm. in diameter packed with glass wool and heated at 400°. Preparative v.p.c. on a dimethylsiloxane polymer column at 106° was used to separate 6 from 8-vinylbicyclo[3.3.0]octene-1.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.56; H, 10.54. Found: C, 89.23; H, 10.50.

The infrared spectrum showed bands at 1645 (s) and 993 cm.$^{-1}$ (s) (vinyl) and also other bands at 822 (s), 878 (w), 997 (s), 1050 (w), 1100 (w), 1293 (w), 1427 (s), 1463 (s), 2875 (s), and 2960 cm.$^{-1}$ (s). The n.m.r. spectrum consisted of multiplets at τ 9.25–9.72 (cyclopropyl methylene H, relative area 4) and 8.63–9.02 (cyclopropyl methyne H, relative area 1), signals centered at τ 7.82 (cyclopentyl methylene H, relative area 4) and 6.95 (cyclopentyl methyne H, relative area 1), and a complex absorption at τ 4.03–5.21 (olefinic H, relative area 4).

8-Vinylbicyclo[3.3.0]octene-1 (7).—Compound 7 was separated from the mixture with 6 as described above. The infrared spectrum showed bands at 1645 (s, C=C stretch) and 995 cm.$^{-1}$ (s, vinyl) and other bands at 800 (s), 910 (s), 1172 (w), 1227 (w), 1322 (w), 1455 (s), 2895 (vs), and 2980 cm.$^{-1}$ (vs). The n.m.r. spectrum consisted of complex absorptions at τ 6.98–8.97 (methylene and methyne protons, relative area 10) and 4.10–5.28 (olefinic protons, relative area 4).

Anal. Calcd. for $C_{10}H_{14}$: C, 89.56; H, 10.54; mol. wt., 134. Found: C, 89.22; H, 10.59; mol. wt. (ebullioscopic), 134.

2-Ethylbicyclo[3.3.0]octane.—Compound 7 was hydrogenated with sodium borohydride in ethanol in a Brown[2] apparatus. A rate plot of the reaction showed two different rates of hydrogenation as expected from the structure of 7. After removal of ethanol, the product was isolated by preparative v.p.c. on a dimethylsiloxane polymer column: b.p. 172.5° (750 mm.).

(8) S. Kh. Begidov, T. V. Domareva, and I. A. D'yakonov, *Zh. Obshch. Khim.*, **33**, 3426 (1963).

(9) R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc.*, **81**, 6443 (1959).

The n.m.r. spectrum had a signal centered at τ 7.51 (assigned to bridge hydrogens in bicyclo[3.3.0]octane,[10] relative area 2), a complex absorption at τ 8.14–8.83 (methylene absorption resembling that in bicyclo[3.3.0]octane,[10] relative area 13), and a well-defined triplet centered at τ 9.03 (methyl H, relative area 3).

Anal. Calcd. for $C_{10}H_{18}$: C, 86.98; H, 13.04. Found: C, 86.90; H, 13.10.

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(10) W. B. Moniz, Ph.D. Thesis, Pennsylvania State University, 1960.

Linear Dimerization of Butadiene with Ferric Chloride–Triphenylphosphine–Triethylaluminum Catalysts
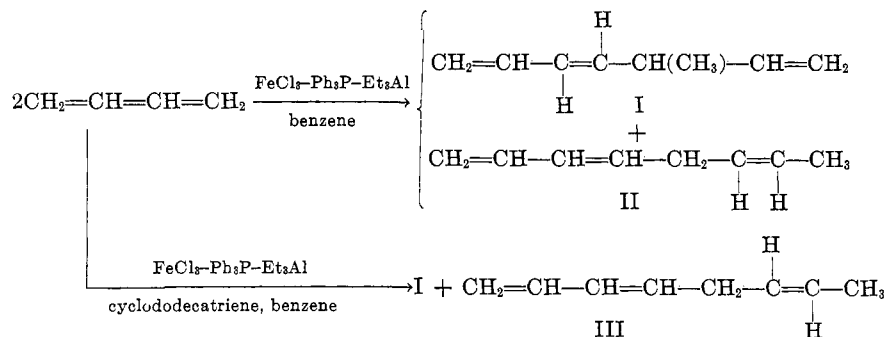
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In the previous paper,[1] it has been reported that butadiene has been cyclotrimerized with a novel catalyst system of alkylaluminum halide–titanium tetraalkoxide. Recently, linear dimers of butadiene, 3-methyl-1,4,6-heptatriene and 1,3,6-octatriene, have been produced upon treatment of butadiene with catalyst systems which consisted of combinations of cobalt compounds and trialkylaluminum.[2] We have now found that novel catalyst systems consisting of combinations of ferric chloride, triphenylphosphine, and alkylaluminum compounds are active for linear dimerization of butadiene.

A catalyst was prepared with 1 mole of anhydrous ferric chloride, 1 mole of triphenylphosphine, and 4 moles of triethylaluminum under a nitrogen atmosphere and shaken with butadiene in an autoclave at room temperature overnight. Distillation of the reaction products gave a dimer fraction in 85% yield based on the fixed butadiene, a trimer fraction in about 5% yield, and high boiling oligomers. The dimer fraction consisted of 3-methyl-1,4,6-heptatriene (about 30%) boiling at 115° and 1,3-*cis*-6-octatriene (about 70%)

boiling at 129°. Infrared, ultraviolet, and n.m.r. spectra of the methylheptatriene were identical with spectra reported by Otsuka[2a] and Misono.[2b] 1,3-*cis*-6-Octatriene absorbed 3 moles of hydrogen upon catalytic hydrogenation over palladium on charcoal. Its infrared and ultraviolet spectra were identical with those reported by Misono.[2b] The n.m.r. spectrum gave a doublet absorption of the methyl group ($=CH–CH_3$) and a triplet absorption of the methylene group. The octatriene gave an adduct of maleic anhydride in quantitative yield.

A catalyst which consisted of a combination of *cis,trans,trans*-1,5,9-cyclododecatriene, anhydrous ferric chloride, triphenylphosphine, and triethylaluminum also dimerized butadiene, giving a mixture of 3-methyl-1,4,6-heptatriene and 1,3,6-octatriene fractions. The octatriene fraction boiling at 129° showed infrared absorptions of vinyl and *trans* double bonds and a trace of a *cis* double bond. The ultraviolet spectrum showed that it had two conjugated double bonds. Its n.m.r. spectrum showed absorptions of the methyl group ($=CH–CH_3$), methylene group, and olefinic protons. The fraction was analyzed by gas chromatography using a tricresyl phosphate column, giving a single peak identical with that of 1,3-*cis*-6-octatriene (II). From these facts, the 1,3,6-octatriene fraction seems to consist of mainly 1,3-*trans*-6-octatriene (III).

The trimer fraction boiling at 140° (15 mm.) absorbed 4 moles of hydrogen upon catalytic hydrogenation over palladium on charcoal and showed infrared absorptions of vinyl, *trans*, and *cis* double bonds. Accordingly, the trimer seems to be linear.

The effects of reaction variables on yields of the dimers have been examined. As summarized in Table I, triethylaluminum and diethylaluminum chloride were equally active. The mole ratio of alkylaluminum compounds to iron compounds must be greater than 3. When the mole ratio was less than 3,

little butadiene dimerized and, at a mole ratio of 4 or higher, the reaction rate of butadiene was increased appreciably and the yields of the dimers were greatly improved. The yields remained approximately constant at higher mole ratios. Instead of anhydrous ferric chloride, iron trisacetylacetonate and iron pentacarbonyl were used successfully. By examination of many electron-donor compounds such as ethers, amines, phosphites, and phosphines, it was found that triphenylphosphine gave the most active catalyst and the mole ratio of triphenylphosphine to iron compounds must be 1 or higher. When no electron-donor compound was used, small amounts of polymer were produced instead of the dimers.

(1) H. Takahasi and M. Yamaguchi, *J. Org. Chem.*, **28**, 1409 (1963).

(2) (a) S. Otsuka, T. Taketomi, and T. Kikuchi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **66**, 1094 (1963); (b) T. Saito, T. Ono, T. Uchida, and A. Misono, *ibid.*, **66**, 1099 (1963); (c) D. W. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); (d) S. Tanaka, K. Mabuchi, and N. Simazaki, the 12th Annual Meeting of Polymer Society of Japan, 1963; (e) Studiengesellschaft Kohle m.b.H., Austrian Patent 219,580 (1962). This catalyst consists of a combination of iron trisacetylacetonate, triphenylphosphine, and diethylaluminum ethoxide gave the methylheptatriene, 4-vinylcyclohexene, and small amounts of cyclooctadiene.