cis-6α-**Isopropyl-9β-methyl-3-decalone.**—A solution of 2.347 g (0.0115 mole) of 10β-methyl-7α-isopropenyl-$\Delta^{1(9)}$-octal-2-one[45] in 40 ml of ethyl acetate was shaken with 230 mg of 10% palladium on charcoal and hydrogen under an initial pressure of 21.5 psi. After 2 equiv of hydrogen were absorbed (40 min), the reaction mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure to afford 2.35 g of a viscous oil, which was chromatographed on 60 g of alumina (Woelm neutral, activity II). The product eluted with 230 ml of *n*-pentane was collected after 80 ml of the first pentane eluate was rejected on the basis of thin layer chromatography. The resulting product could not be sublimed at 42° (0.1 mm) as described in the literature.[46] However, by repeated low-temperature crystallization (acetone–Dry Ice) from *n*-pentane, a small amount (12 mg) of pure *cis*-6α-isopropyl-9β-methyl-3-decalone (*cis*-7α-isopropyl-10β-methyl-2-decalone) was obtained, mp 55.5–57.0° (lit.[46] 55–57°), single peak in glpc.[46]

(45) J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, **31**, 1016 (1966).

(46) C. Djerassi, J. Burakevich, J. W. Chamberlin, D. Elad, T. Toda, and G. Stork, *J. Am. Chem. Soc.*, **86**, 465 (1964). The yield of the pure compound is not mentioned in this paper.

Acknowledgment.—We are grateful to the following persons for kindly donating the compounds noted: W. Nagata (**7, 10, 26g, 29**), T. Komeno (**24k, 56**), and S. Nakajima (**20a–b, 22b, 24e,h, 26e, i, j**), all of Shionogi and Company, Ltd.; M. Yanagita (**12, 14**); R. B. Woodward (**14**); T. Reichstein (**16**); G. von Mutzenbecher (**18**) and J. A. Edwards (**22a**) of Syntex; John Fried of Syntex and H. J. Ringold (**24g, 56**); E. R. H. Jones (**26h**); A. Wettstein (**27a**) of CIBA Ltd.; L. F. Fieser (**27b-c**); H. L. Slates (**22c**) and D. Taub (**32**) of Merck and Company; O. A. de Bruin of N. V. Philips-Duphar (lumisterol); D. H. R. Barton (hecogenin acetate); J. Fishman (**37, 37a**); R. Sciaky (**24i**); A. K. Bose (**24j**); Josef Fried (**24l, 44**); E. Havinga (**43**); W. H. Baarschers (**45**); P. A. Diassi (**50a–c**) of The Squibb Institute for Medical Research; Y. Mazur (**52a–b, 54a–b**); J. A. Marshall (**61–63**, and 10β-methyl-7α-isopropenyl-$\Delta^{1(9)}$-octal-2-one); and M. P. Cava (**18a**).

The Synthesis of Steroidal Cyclopropano Ketones

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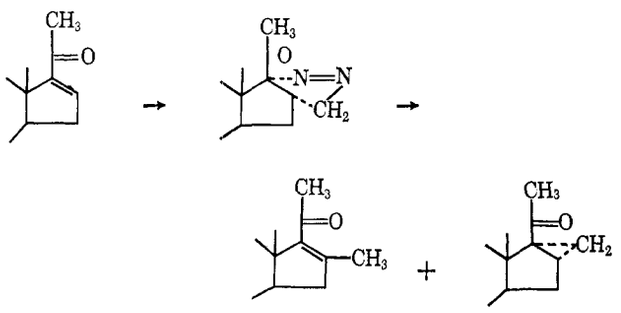
The ylide, dimethylsulfoxonium methylide, has been shown to react with steroidal $\Delta^{1,4,6}$-, $\Delta^{4,6}$-, and 19-nor-Δ^{4}-3-ones to give the corresponding 1α,2α-, 6α,7α-, and 4β,5β-methylene derivatives, respectively. The preparation of cyclopropano steroids by this method is compared with the sequence unsaturated ketone → pyrazoline → cyclopropano steroid. The ORD, nmr, and other physical properties of these compounds are described.

The formation of a steroidal pyrazoline by the addition of diazomethane to a Δ^{16}-20-one was first reported by Wettstein[1] in 1944. The thermal decomposition of this system gave as the major product the 16-methyl-Δ^{16}-20-one and a minor product which was subsequently shown[2] to be the 16,17-methylene-20-one (see Scheme I).

SCHEME I



In 1960, Wiechert and Kaspar[3] extended this reaction to the $\Delta^{1,4,6}$-3-one system. They found that the pyrazoline formed in this case could be converted in good yield to the 1,2-methylene-$\Delta^{4,6}$-3-one. The addition of diazomethane was assumed to take place from the less hindered α side of the molecule and therefore the placement of the pyrazoline and methylene rings was considered to be 1α,2α.

Our interest in modifying the structure of physiologically active steroids led us also to utilize the addition of diazomethane to the $\Delta^{1,4,6}$-3-one moiety as a means of preparing 1,2-methylene compounds. Thus, as was reported,[3] we found that the 1α,2α-pyrazoline derivative (**2**) formed from 16α,17α-(dimethylmethylenedioxy)-1,4,6-pregnatriene-3,20-dione[4] (**1**) could be converted thermally or by acid-catalyzed decomposition to 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (**4**). The over-all yield of **4** prepared by the perchloric acid–acetone decomposition of the pyrazoline was 23%. The possible utility of this sequence for the preparation of substituted 1α,2α-methylene derivatives was investigated by treating diazoethane[5] with **1**. The resulting 5-methylpyrazoline derivative **3**, was obtained in 25% yield and, in analogy with the previous assignments, given the 1α,2α configuration. While the ultraviolet absorption spectrum of **2** had the expected[3] peaks at 235 mμ (ε 4000) and 293 mμ (ε 21,800), the more highly substituted pyrazoline **3** had only the higher wavelength peak at 289 mμ (ε 21,000). The infrared spectra of the pyrazolines showed the N=N stretching peak at 6.48 μ (1543 cm^{-1}) in **2** and 6.50 μ (1538 cm^{-1}) for **3**, in addition to the peaks expected for a $\Delta^{4,6}$-3-one system at 6.06, 6.19, and 6.33 μ.[6] The nmr spectrum of **3** exhibited a doublet at τ 8.71 (J = 7.7 cps) resulting from the methyl attached to the pyrazoline ring. This doublet collapsed to a singlet when a spin-decoupling experiment[7] was carried out and the sample irradiated 235 cps downfield. Spin decoupling also

(1) A. Wettstein, *Helv. Chim. Acta*, **27**, 1803 (1944).

(2) A. Sandoval, G. Rosenkranz, and C. Djerassi, *J. Am. Chem. Soc.*, **73**, 2383 (1951).

(3) R. Wiechert and E. Kaspar, *Chem. Ber.*, **93**, 1710 (1960).

(4) U. S. Patent 3,174,971 (March 23, 1965).

(5) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

(6) G. R. Allen, Jr., and M. J. Weiss, *J. Am. Chem. Soc.*, **82**, 2840 (1960).

(7) We wish to thank Mr. G. D. Vickers, Olin Mathieson Chemical Corp., New Haven, Conn., for his assistance in performing this experiment on a Varian Associates HR-60 instrument.

permitted the assignment of the other protons in the pyrazoline system. The proton attached to the 5′ position of the pyrazoline appeared as a complex multiplet at $\sim\tau$ 4.8 and was coupled to the 5′-methyl group as well as the 2β hydrogen. This latter proton exhibited a quartet (J = 1.5, 6 cps) coupled to the 5′ hydrogen and the adjacent 1β hydrogen. This 1β proton appeared as a doublet at τ 7.40 (J = 6 cps).

On perchloric acid–acetone or boron trifluoride–ether treatment of **3**, there was no evidence of nitrogen evolution. The noncrystalline material isolated from these reactions still contained nitrogen and was undoubtedly a mixture of double-bond isomers of the starting material. Thus, we did not succeed in preparing any substituted methylene derivatives.

When diazomethane was treated with 6-chloro-16α-17α-(dimethylmethylenedioxy)-1,4,6-pregnatriene-3,-20-dione[8] (**9**) a poor yield (<10%) of the pyrazoline **10** was obtained. Its spectral features were consistent with the assigned structure. The infrared spectrum had peaks at 5.85 (20-ketone), 6.02, 6.25, and 6.33 ($\Delta^{4,6}$-3-one system), and 6.48 μ (N=N) and it absorbed in the ultraviolet at 235 mμ (ϵ 5000) and 293 mμ (ϵ 16,100). Treatment of the pyrazoline **10** with perchloric acid–acetone gave a small amount of a new compound whose structure was ultimately shown to be the corresponding 1α,2α-methylene derivative **8** (see below). Only recovered starting material was obtained when 16α,17α-(dimethylmethylenedioxy)-1,4-pregnadiene-3,20-dione[6] (**13**) was treated with diazomethane.

Ylide Reaction.—In 1962, Corey and Chaykovsky[9] published a preliminary report on the preparation and use of a new reagent, dimethylsulfoxonium methylide. In a formal sense, this reagent added methylene to a carbonyl to give the oxirane and to an α,β-unsaturated carbonyl to give the corresponding cyclopropane derivative. In this report and in a subsequent publication,[10] it was mentioned that cholestenone was recovered unchanged from reaction with the methylide. Recently, it has been reported[11] that this reagent will convert a conjugated steroidal methylene ketone to the corresponding cyclopropyl derivative. Thus, in the basic medium of dimethylsulfoxonium methylide the methiodide of a 2-dimethylaminomethyl-3-one eliminated amine to give 2-methylene-3-one which reacted *in situ* with the methylide to give 2-spirocyclopropyl-3-one. Various groups[12] have also used the methylide to prepare steroidal spirooxiranyl derivatives from the corresponding ketones.

We have found that dimethylsulfoxonium methylide will react with suitable "unhindered" steroidal conjugated ketones. Thus, treatment of trienone **1** with this methylide gave a 50–60% yield of the previously described 1α,2α-methylene derivative **4**. Since, (see the Experimental Section) 6-chloro-16α,17α-(dimethylmethylenedioxy)-1,4,6-pregnatriene-3,20-dione[8] (**9**) gave a complex mixture on treatment with dimethylsulfoxonium methylide, an alternate scheme was used to prepare the 6-chloro-1α,2α-methylene derivative **8**. Treatment of **4** with *m*-chloroperbenzoic acid gave the expected 6α,7α-epoxide **5** in 60% yield. The α addition of oxygen is based on the analogous α attack on unsubstituted $\Delta^{4,6}$-3-ones[13,14] as well as on the course of the subsequent reaction of this epoxide. The deshielding of the 4 proton by 0.4 ppm in the nmr spectrum on introduction of the epoxide group also supports this assignment. Treatment of the epoxide **5** with 1 equiv of hydrogen chloride in chloroform at 0°, gave the expected chlorohydrin **6**. When either the chlorohydrin **6** or the epoxide **5** was treated with chloroform saturated with hydrogen chloride at room temperature, elimination of the oxygen function took place and a 6-chloro-$\Delta^{4,6}$-3-one moiety was introduced. In addition to this, the cyclopropane ring was opened under these conditions and instead of the expected product **8**, 6-chloro-1α-chloromethyl-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,-20-dione (**7**) was obtained in 70% yield. When a solution of **7** in collidine was refluxed under helium for 3 hr, ring closure with elimination of the elements of hydrogen chloride took place and a 70% yield of 6-chloro-1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione **8** was obtained. The placement of the chloromethyl group at C-1 is based on similar opening of a cyclopropane ring in other systems.[15] The alternate structure, having the equatorial 2α-chloromethyl group is extremely unlikely as base treatment of this moiety would be expected to lead to a 2-methylene derivative, rather than the obtained cyclopropane ring closure. The infrared spectrum of the previously described product obtained from decomposition of the pyrazoline **10** was identical with that of the present preparation. This substance absorbed in the ultraviolet at 280 mμ (ϵ 16,100). (See Scheme II.)

Scope of the Ylide Reaction.—Since dimethylsulfoxonium methylide was found to insert a methylene into **1**, we decided that it would be of interest to see to what extent this ylide reacted with other conjugated 3-ketones. In confirmation of the previously reported[7,8] inertness of cholestenone to this reagent, we found that 16α,17α-(dimethylmethylenedioxy)-4-pregnene-3,20-dione (**11a**)[16] did not react when treated with the ylide. The vapor phase chromatogram of the colored material recovered from the reaction mixture

(8) This compound was prepared by reaction of **14** with *m*-chloroperbenzoic acid followed by hydrogen chloride–chloroform treatment of the resulting 6α,7α-epoxide. The 6-chloro-6-dehydro compound obtained was then converted to **9** by DDQ–dioxane dehydrogenation (unpublished results from these laboratories).

(9) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).

(10) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

(11) H. R. Lehmann, H. Muller, and R. Wiechert, *Chem. Ber.*, **98**, 1470 (1965).

(12) (a) M. E. Wolff, W. Ho, and R. Kwok, *J. Med. Chem.*, **7**, 577 (1964); (b) H. G. Lehmann, O. Engelfried, and R. Wiechert, *ibid.*, **8**, 383 (1965); (c) C. E. Cook, R. C. Corley, and M. E. Wall, *Tetrahedron Letters*, 891 (1965).

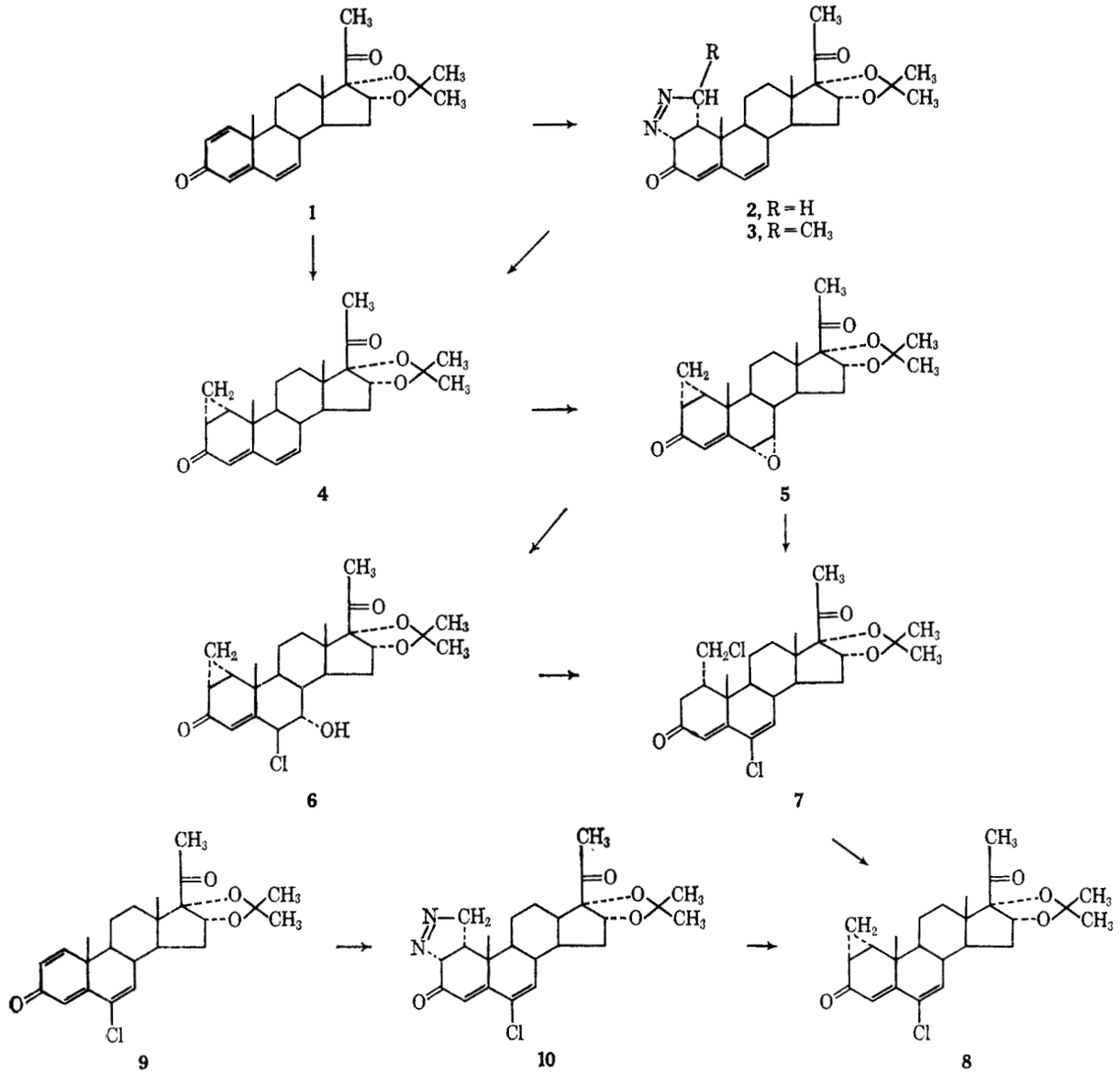
(13) L. H. Knox, J. A. Zderic, J. P. Ruelas, C. Djerassi, and H. J. Ringold, *J. Am. Chem. Soc.*, **82**, 1230 (1960). K. Bruckner, B. Hampel, and U. Johnsen, *Chem. Ber.*, **94**, 1225 (1961).

(14) A. L. Nussbaum, G. Brabazon, T. L. Popper, and E. P. Oliveto, *J. Am. Chem. Soc.*, **80**, 2722 (1958).

(15) (a) A. Baeyer, *Ber.*, **27**, 1915 (1894); **31**, 3208 (1898). H. Carpio, A. C. Bazan, M. G. Teran Medina, and J. A. Edwards [*J. Org. Chem.*, **30**, 4154 (1965)] present an example of the opening of a 5β,19-cyclo-6-one to a 19-chloromethyl derivative. The chloromethyl protons in their case appear as an AB pattern centered at 217 cps (τ 6.38). In our case the protons of the chloromethyl group are further coupled and appeared as a complex poorly resolved multiplet centered at τ 6.46 in the nmr spectrum. (b) We appreciate being informed by a referee that opening of the 1,2-methylene group has been described in the patent literature. See R. Wiechert, West German Patent 1,122,944 (April 6, 1960); R. Wiechert, U. S. Patent 3,234,093, (Feb 8, 1966).

(16) G. Cooley, F. Hartley, B. Ellis, and V. Petrow, *J. Chem. Soc.*, 4373 (1955).

SCHEME II



showed over 90% of starting material. Thin layer chromatography on silica gel also indicated only starting material and a small amount of some highly polar material remaining at the origin. When the ylide was treated with 16α,17α-(dimethylmethylenedioxy)-1,4-pregnadiene-3,20-dione[6] (**13**), the vapor phase chromatogram of the crude reaction product showed the presence of approximately 25% of a more polar compound, 65% of starting material, and 10% of minor constituents. The retention time of the more polar compound was identical with that of authentic 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4-pregnene-3,20-dione (**16**) prepared independently (see below). This mixture could not be resolved by crystallization and since **16** was available by an alternate procedure, additional effort was not expended in this direction. (See Scheme III.)

Treatment of 16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione[6] (**14**) with dimethylsulfoxonium methylide gave an 18% yield of the 6,7-methylene derivative (**15**). This compound absorbs in the ultraviolet at 267 mμ (ε 16,600), another example of a cyclopropane ring extending the conjugation of an α,β-unsaturated ketone.[17] The nmr spectrum of **15** no longer shows the presence of the 6,7-vinyl protons. The orientation of the methylene group is believed to be 6α,7α in analogy to the generally observed backside attack to the 6,7 double bond.[14,18]

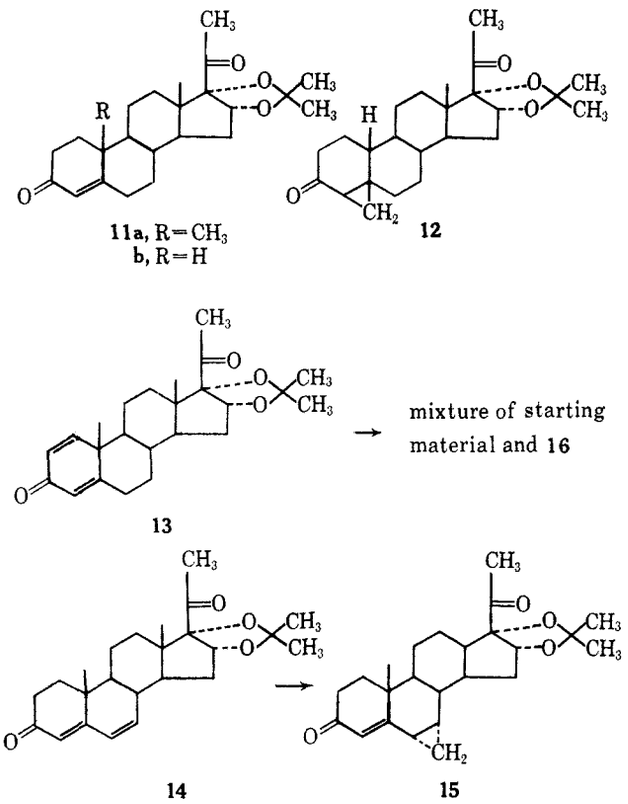
In consequence of the lack of reactivity of the Δ^4-3-ones to the ylide, it was especially interesting to find that the 19-nor-Δ^4-3-one **11b**[19] reacted with this reagent to give a product which has no specific absorption in the ultraviolet. After thin layer chromatography of this product a 40% yield of the 4,5-methylene derivative **12** was obtained. This compound showed only end

(17) R. B. Bates, G. Buchi, T. Matsuura, and R. R. Shaffer, *J. Am. Chem. Soc.*, **82**, 2327 (1960); R. S. Irvine, J. A. Henry, and F. S. Spring, *J. Chem. Soc.*, 1316 (1955).

(18) (a) L. Fieser, *Experientia*, **6**, 312 (1950). (b) After the completion of this paper, a communication appeared [N. H. Dyson, J. A. Edwards, and J. H. Fried, *Tetrahedron Letters*, 1841 (1961)] in which the reaction of $\Delta^{4,6}$-diene-3-ones with dimethylsulfoxonium methylide was described. In two cases mixtures of 6α,7α- and 6β,7β-methylene derivatives were obtained while in one case a single 6,7-methylene compound was observed. These authors prefer as we do to assign the 6α,7α stereochemistry to this compound. The shielding effect of τ 0.11 (6.5 cps) of the 6,7-methylene group on the C-19 protons of unsubstituted **11a** seen in our case is entirely consistent with the reported shielding of 7–8 cps of these authors.

(19) Belgium Patent 621,042 (Feb 4, 1963).

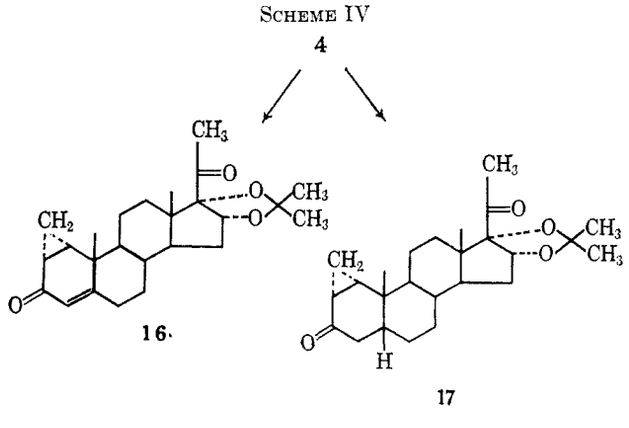
SCHEME III



absorption in the ultraviolet and did not exhibit any vinyl proton resonance in its nmr spectrum. Since the starting material **11b** does not possess the angular methyl group at C-10, which is responsible for shielding the β side of normal steroids from attack,[18] it is difficult to predict *a priori* what the orientation of the methylene group in **12** is. Indeed, as will be shown below, an ORD determination indicates that this methylene is attached $4\beta,5\beta$.

Physical Properties and Stereochemistry.—The stereochemistry of the 1,2-methylene derivatives described in this paper has been assumed to be $1\alpha,2\alpha$. This is based, of course, on the usual preference for attack from the rear on steroids bearing the angular methyl groups at C-10 and C-13.[18] However, since the mechanism of the reaction of dimethylsulfoxonium methylide and conjugated carbonyl compounds has not been clearly established,[10] we felt that an additional demonstration of this assignment was in order. The recent publication by Djerassi, *et al.*,[20] concerning the optical rotatory dispersion of cyclopropyl and epoxy ketones enabled us to use this tool to unambiguously assign the configuration of the 1,2-methylene group. These authors conclude that the "octant rule"[21] can be applied to saturated cyclopropyl ketones but that the sign of the octants must be reversed. We therefore, catalytically reduced the unsaturated cyclopropyl ketone **4**. When **4** was hydrogenated in alkaline medium using a palladium catalyst,[22] the partially reduced **16** was obtained if the reduction was stopped after 1 equiv of hydrogen was taken up. This compound absorbed in the ultraviolet at 240 mμ (ϵ 12,500) and its nmr spectrum showed the presence of one vinyl proton. When **4** was hydrogenated under similar conditions until the uptake of hydrogen ceased, the saturated cyclopropyl ketone **17** was obtained. This compound no longer had any selective absorption in the ultraviolet and its nmr spectrum showed the absence of vinyl protons. The stereochemical course of this reduction was not *a priori* predictable. Although, it is known[23] that partial reduction of Δ^4-3-ones with palladium gives the 5β-3-one, the presence of the 1,2-methylene group is a potentially complicating factor. Fortunately, the reasoning involved in the assignment of the stereochemistry of the latter group does not depend on the nature of the A/B ring juncture. If the methylene group is oriented $1\alpha,2\alpha$ then regardless of whether the A/B juncture in **17** is *cis* or *trans*, the cyclopropyl ring will lie in the back lower left octant for which the octant rule[20] predicts a positive Cotton effect. On the other hand, if the methylene group is oriented $1\beta,2\beta$ then it is located in the back upper left octant, irrespective of the geometry of the A/B ring juncture and its Cotton effect would be negative. The ORD curve of **17** is shown in Figure 1 and since it is positive, we can assign the α configuration to the methylene group. Once this assignment is made, it seems reasonable to assume that the hydrogenation of **4** led to the 5β derivative since approach of the catalyst and hydrogen from the α side is even less likely than for an unsubstituted Δ^4-3-ketone. Therefore, the complete structure of **17** is $1\alpha,2\alpha$-methylene-$16\alpha,17\alpha$-(dimethylmethylenedioxy)-5β-pregnane-3,20-dione. (See Scheme IV.)

SCHEME IV



Using this technique we have been able to assign the stereochemistry of the 4,5-methylene derivative **12** as well. An α-oriented methylene is located in the lower right negative octant, whereas, a β-methylene derivative occupies an upper right positive octant. In Figure 1 the ORD curve of **12** is shown and since it is a positive curve we have assigned this compound the $4\beta,5\beta$ structure.

In Table I are listed the molecular rotation differences observed on introduction of the $1\alpha,2\alpha$-methylene moiety. From this table we can see a consistent dextrorotatory effect upon introduction of a $1\alpha,2\alpha$ methylene into Δ^4- or $\Delta^{4,6}$-3-ketones.

(20) C. Djerassi, W. Klyne, T. Norin, G. Ohloff, and E. Klein, *Tetrahedron*, **21**, 163 (1965); see also K. Schaffner and G. Snatzke, *Helv. Chim. Acta*, **48**, 347 (1965), who come to similar conclusions based on circular dichroism measurements.

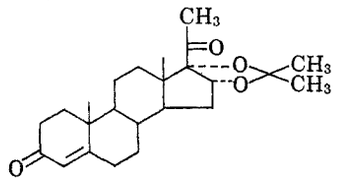
(21) W. Moffit, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

(22) A. F. Daglish, J. Green, and V. D. Poole, *J. Chem. Soc.*, 2627 (1954); D. A. Shepherd, *et al.*, *J. Am. Chem. Soc.*, **77**, 1212 (1955).

(23) H. Grasshof, *Z. Physiol. Chem.*, **223**, 249 (1934).

TABLE I

MOLECULAR ROTATION DATA OF 1α,2α-METHYLENE DERIVATIVES[a]



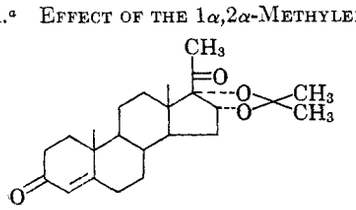
Substituents	MD, deg	MD, 1α,2α-CH2, deg	ΔMD, deg
...	+518[b]	+1060	+542
6-Dehydro	+281[c]	+747	+466
6α,7α-Oxido	+332[d]	+927	+595
6β-Chloro-7α-hydroxy	+262[d]	+889	+627
6-Chloro-6-dehydro	+352[d]	+879	+527

[a] All rotations are reported in chloroform. [b] Reference 16. [c] Reference 6. [d] Unpublished results from these laboratories.

The effects of the 1α,2α-methylene group on the nmr frequencies of the proton attached to C-19 and the C-4 vinyl proton are shown in Table II. A slight de-

TABLE II

NMR DATA.[a] EFFECT OF THE 1α,2α-METHYLENE GROUP



Substituent	C-19 protons, 1,2-CH2	C-4 protons, 1,2-CH2
...[b]	8.80,[c] 8.71	4.27,[c] 4.46
6-Dehydro[d]	8.87,[c] 8.79	4.30,[c] 4.48
6α,7α-Oxido	8.88,[c] 8.81	3.87,[c] 4.02
6β-Chloro-7α-hydroxy	8.58,[c] 8.49	4.05,[c] 4.18
6-Chloro-6-dehydro	8.83,[c] 8.78	3.68,[c] 3.82

[a] Spectra were determined in deuteriochloroform and are reported in τ units. [b] Reference 16. [c] Unpublished results from these laboratories. [d] Reference 6.

shielding of 0.05–0.09 ppm is observed for the C-19 protons. The vinyl proton at C-4 on the other hand is shielded by the methylene group by 0.13–0.19 ppm.

Experimental Section[24]

General Procedure for Preparation and Reactions of Dimethylsulfoxonium Methylide.—Solutions of dimethylsulfoxonium methylide were prepared by treating a solution of trimethylsulfoxonium iodide[25] in dimethyl sulfoxide (10% v/v) with an equivalent amount of sodium hydride powder or 50% sodium hydride in mineral oil.[26] The mixture was stirred at room temperature under an atmosphere of nitrogen until the evolution of hydrogen ceased. Two to five molar excesses of the ylide were used to add methylene to the appropriate unsaturated ketones.

(24) Melting points are uncorrected. Solutions were dried over magnesium sulfate prior to evaporation. Optical rotations were taken in chloroform solution at 20–25° (c 0.5–1.0). Rotations given for more than one wave length were taken on a Perkin-Elmer Model 141 polarimeter. Ultraviolet spectra were recorded as ethanol solutions on a Cary 11 spectrometer and infrared spectra were recorded on potassium bromide disks on a Perkin-Elmer Model 21 spectrophotometer. Nuclear magnetic resonance spectra were measured in deuteriochloroform solution using tetramethylsilane as an internal standard on a Varian Associates A-60. Vapor phase chromatographic analyses were determined on an F & M Model 1609 using a 5.5 ft × 3/16 in. column packed with 0.2% (w/w) Carbowax 20 M on 70–80 mesh Anakrom ABS.

(25) R. Kuhn and H. Trishmann, *Ann. Chem.*, **611**, 117 (1958).

(26) Metal Hydrides Inc., Beverly, Mass.

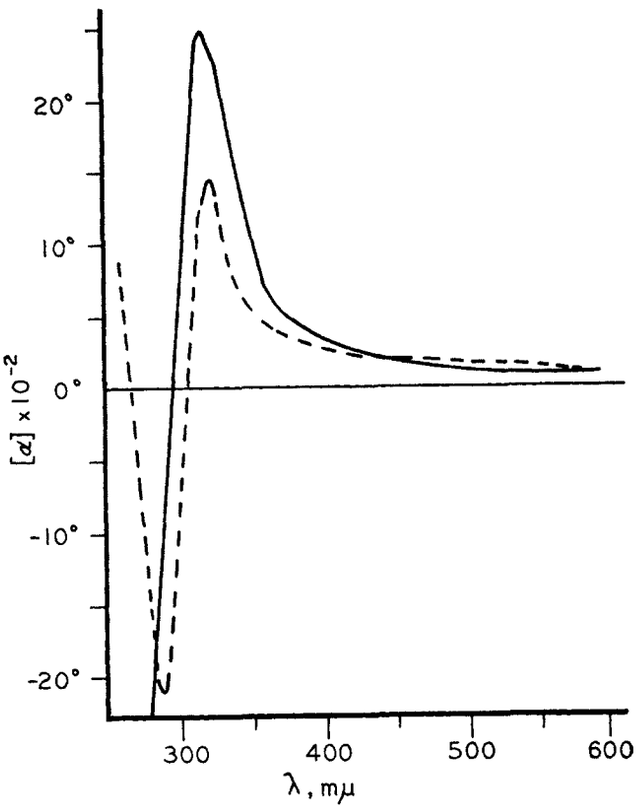


Figure 1.—Optical rotatory dispersion curves of 4β,5-methylene-16α,17α-(dimethylmethylenedioxy)-19-nor-5β-pregnane-3,20-dione (**12**) (--------) and 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-5β-pregnane-3,20-dione (**17**) (———).

The most convenient way to do this was to add the compound to the required amount of freshly prepared ylide solution and stir at room temperature under nitrogen overnight. The reaction mixtures were then diluted with water and if a precipitate formed it was filtered and washed well with water and then taken up in ether or ether–ethyl acetate. If no precipitate formed the aqueous reaction mixture was extracted with ether or ethyl acetate. This solution was washed well with water, dried, and evaporated to give a residue usually still containing traces of dimethyl sulfoxide. The products were purified by chromatography on neutral alumina (activity I) or by thin layer chromatography on neutral alumina (activity V).

16α,17α-(Dimethylmethylenedioxy)-1α,2α-(4′,3′,1′-pyrazolino)-4,6-pregnadiene-3,20-dione (2).—A solution of 120 ml of ether containing 13 mmoles of diazomethane was added to 450 mg of 16α,17α-(dimethylmethylenedioxy)-1,4,6-pregnatriene-3,20-dione[4] (**1**, 1.2 mmoles). After 2 days at room temperature, yellow, crystalline material settled out and was collected by centrifugation. After washing with ether and drying, this material weighed 206 mg and had a melting point of 259–260° dec; λ_{max} 230 mμ (flat) (ε 5800), 293 mμ (ε 20,400). The centrifugate was left at room temperature for an additional 3 days whereupon an additional 194 mg of 16α,17α-(dimethylmethylenedioxy)-1α,2α-(4′,3′,1′-pyrazolino)-4,6-pregnadiene-3,20-dione (**2**), mp 240–243° dec, separated. On recrystallization from methanol this latter material gave 94 mg of product which had mp 261–262° dec. The analytical sample had a melting point of 262–263° dec; $[\alpha]_D$ −22°; λ_{max} 5.86, 6.06, 6.19, 6.33 μ; λ_{max} 235 mμ (ε 4000), 293 mμ (ε 21,800); nmr[27] τ 9.30 (18-H, s), 8.75 (19-H, s), 4.91 (16β-H, d, J = 4 cps), 4.13 (4-H, s), 3.81 (6- and 7-H, s).

Anal. Calcd for $C_{25}H_{32}N_2O_4$: C, 70.72; H, 7.60, N, 6.60. Found: C, 70.56; H, 7.66; N, 6.87.

16α,17α-(Dimethylmethylenedioxy)-1α,2α-(4′,3′,5′-methyl-1′-pyrazolino)-4,6-pregnadiene-3,20-dione (3).—A solution of 165

(27) The resonance peaks for the 21 protons and the acetonide protons have not been included in the data presented here. The 21 protons appear as a singlet appearing between τ 7.73 and 7.78. The acetonide protons appear as two singlets, the higher field signal at τ 8.79–8.82, and the other at 8.47–8.52. These signals have been assigned to the β- and α-methyl groups, respectively. In the reporting of the nmr data, as is customary, s = singlet, d = doublet, m = multiplet, and br = broad.

ml of ether containing 23 mmoles of diazoethane[5] was added to 852 mg of 16α,17α-(dimethylmethylenedioxy)-1,4,6-pregnatriene-3,20-dione[4] (1). After 4 days at room temperature, the excess diazoethane was removed by entrainment with helium and the ether evaporated. The resulting residue was recrystallized from methanol to give 159 mg of 16α,17α-(dimethylmethylenedioxy)-1α,2α(4′,3′,5′-methyl-1′-pyrazolino)-4,6-pregnadiene-3,20-dione (3), mp 220–221° dec. The analytical sample had mp 221–221.5° dec; $[\alpha]_D$ +153°; λ_{max} 5.85, 6.05 (br), 6.19, 6.30, 6.50 μ; λ_{max} 289 mμ (ε 21,000); nmr τ 9.24 (18-H, s), 8.69 (19-H, s), 4.91 (16β-H, d, J = 4.5 cps), 4.35 (4-H, s), 3.83 (6- and 7-H, s), 8.71 (5′-CH_3, d, J = 7.5 cps), 4.73 (1′-H, m), 5.53 (2β-H, d, d, J = 1.5, 6.5 cps), 7.40 (1β-H, d, J = 6.5 cps).

Anal. Calcd for $C_{26}H_{34}N_2O_4$: C, 71.20; H, 7.82. Found: C, 71.34; H, 8.03.

1α,2α-Methylene-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (4). A. Acid Decomposition of Pyrazoline.—A solution of 0.50 ml of 70% perchloric acid in 50 ml of acetone was added to 170 mg of 16α,17α-(dimethylmethylenedioxy)-1α,2α-(4′,3′,1′-pyrazolino)-4,6-pregnadiene-3,20-dione (2). The pyrazoline dissolved with evolution of nitrogen and when the evolution of gas ceased (5 min) the reaction mixture was diluted with water and neutralized by the addition of 10% potassium carbonate solution. The acetone was evaporated and the aqueous suspension was extracted with chloroform. After washing the chloroform solution with water and drying, the chloroform was evaporated. Two recrystallizations from methanol gave 57 mg of 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (4): mp 254–255°; $[\alpha]_D$ +191°; λ_{max} 5.86, 6.06, 6.47, 6.31 μ; λ_{max} 282 mμ (ε 20,800); nmr τ 9.30 (18-H, s), 8.79 (19-H, s), 4.93 (16β-H, d, J = 4 cps), 4.48 (4-H, s), 3.98 (6- and 7-H, s).

Anal. Calcd for $C_{25}H_{32}O_4$: C, 75.72; H, 8.13. Found: C, 75.76; H, 8.17.

B. Pyrolysis of Pyrazoline.—Pyrazoline (2, 29 mg) was heated under vacuum in a sublimation tube. At 235 to 245° and 0.001 mm of Hg the sample decomposed with the evolution of gas and sublimed. The sublimate was recrystallized from methanol to give a first crop of 7 mg of starting material and a second crop of 9 mg of 4: mp 253–254°, λ_{max} 284 mμ (ε 19,600).

C. Dimethylsulfoxonium Methylide Method.—16α,17α-(Dimethylmethylenedioxy)-1,4,6-pregnatriene-3,20-dione[4] (1, 3.30 g, 10 mmoles) was added to a solution of 25 mmoles of ylide in 50 ml of dimethyl sulfoxide and stirred for 22 hr. After work-up as described above and chromatography on 100 g of alumina, elution with benzene and benzene–chloroform (4:1) gave 2.83 g of 4 which on recrystallization from methanol furnished 1.18 g of pure material, mp 253–255°.

Treatment of 3 with Perchloric Acid–Acetone.—A solution of 75 mg of 3 in 25 ml of acetone and 0.25 ml of 70% perchloric acid was kept at room temperature for 15 min. The reaction mixture was worked up as described above. After thin layer chromatography on neutral alumina (activity V) in hexane–chloroform (1:4) the major ultraviolet absorbing spot was eluted with ethyl acetate to give 26 mg of yellow oil, λ_{max} 270 mμ ($E^{1\%}$ 344).

Anal. Found: N, 5.77.

1α,2α-Methylene-16α,17α-(dimethylmethylenedioxy)-6α,7α-oxido-4-pregnene-3,20-dione (5).—A solution of 1.00 g of 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (4) and 2.15 g of *m*-chloroperbenzoic acid in 25 ml of methylene chloride was left at room temperature for 22 hr. The reaction mixture was diluted with methylene chloride to a volume of 150 ml and then washed with five 100-ml portions of 5% potassium carbonate, two 100-ml portions of water, 100 ml of 5% potassium iodide solution, 100 ml of water, two 100-ml portions of 5% sodium sulfite solution, and 100 ml of water, dried, and evaporated to give 985 mg of crude product. Recrystallization from methanol gave 679 mg of 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-6α,7α-oxido-4-pregnene-3,20-dione (5): mp 260–262°; $[\alpha]_D$ +226°; λ_{max} 5.84, 6.00 μ; nmr τ 9.32 (18-H, s), 8.81 (19-H, s), 4.89 (16β-H, d, J = 4.5 cps), 4.02 (4-H, s), 6.56 and 6.72 (6- and 7-H, AB, q, J = 4 cps).

Anal. Calcd for $C_{25}H_{32}O_5$: C, 72.79; H, 7.82. Found: C, 72.65; H, 7.80.

6β-Chloro-7α-hydroxy-1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4-pregnene-3,20-dione (6).—A solution of 103 mg of 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-6α,7α-oxido-4-pregnene-3,20-dione (5) in 10 ml of chloroform was cooled to below 5° and treated with 0.9 ml of chloroform containing 1 equiv of hydrochloric acid. The reaction mixture was kept at a temperature below 5° for 2.5 hr and water was then added. The organic layer was separated and washed with water until neutral, dried, and evaporated to give 115 mg of an oil. Crystallization from methanol furnished 75 mg of 6β-chloro-7α-hydroxy-1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4-pregnene-3,20-dione (6), mp 237–239°. A further recrystallization raised the melting point to 238–239.5°; $[\alpha]_D$ +199°; λ_{max} 2.99, 5.85, 6.06 (br) μ; λ_{max} 236 mμ, (ε 16,100); nmr τ 9.29 (18-H, s), 8.49 (19-H, s), 4.93 (16β-H, d, J = 4.5 cps), 4.18 (4-H, s), 5.56 (7β-H, d, J = 2.3 cps), 6.13 (6α-H, m).

Anal. Calcd for $C_{25}H_{33}ClO_5$: C, 66.86; H, 7.41. Found: C, 66.67; H, 7.44.

6-Chloro-1α-chloromethyl-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (7). A.—A solution of 588 mg of 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-6α,7α-oxido-4-pregnene-3,20-dione (5) in 60 ml of chloroform saturated with hydrogen chloride was kept at room temperature for 4 hr. Water was then added and after vigorous shaking the chloroform layer separated. The organic solution was washed with 5% bicarbonate solution and water, dried, and evaporated to give 670 mg of crude product. On recrystallization from methanol, 397 mg of 7, mp 279–282°, was obtained. Further recrystallization gave analytically pure material: mp 292–294°; $[\alpha]_{589}$ +21°, $[\alpha]_{578}$ +21°, $[\alpha]_{546}$ +32°, $[\alpha]_{436}$ +245°, $[\alpha]_{365}$ −173°; λ_{max} 5.85, 6.00, 6.25, 6.34 μ; λ_{max} 287 mμ (ε 22,400); nmr τ 9.30 (18-H, s), 8.69 (19-H, s), 4.89 (16β-H, d, J = 5 cps), 3.61 (4-H, s), 3.65 (7-H, m).

Anal. Calcd for $C_{25}H_{32}Cl_2O_4$: C, 64.23; H, 6.90; Cl, 15.17. Found: C, 64.56; H, 6.88; Cl, 15.69.

B.—A solution of 50 mg of 6β-chloro-7α-hydroxy-1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4-pregnene-3,20-dione (6) in 5 ml of chloroform saturated with hydrogen chloride was treated and worked up as described above to give 52 mg of crude product. Recrystallization from methanol gave 29 mg of 7 identical by melting point and infrared spectrum with authentic material.

6-Chloro-1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (8). A.—A solution of 408 mg of 6-chloro-1α-chloromethyl-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (7) in 25 ml of Swiss collidine (distilled and stored over potassium hydroxide) was refluxed for 3 hr with a stream of helium bubbling through the solution. The reaction mixture was poured into 250 ml of cold 5% hydrochloric acid and extracted with ether–methylene chloride (2:1). The organic solution was washed with 5% hydrochloric acid and saturated salt solution until neutral, dried, and evaporated to give 419 mg of crude product. Recrystallization from methanol gave a first crop of 272 mg of 8, mp 298–302°, and a second crop of 45 mg, mp 295–297°. The analytical sample had mp 302–303°; $[\alpha]_{589}$ +204°, $[\alpha]_{578}$ +220°, $[\alpha]_{546}$ +275°, $[\alpha]_{436}$ +884°; λ_{max} 5.86, 6.00 (br), 6.20, 6.29 μ; λ_{max} 280 mμ (ε 16,600); nmr τ 9.31 (18-H, s), 8.78 (19-H, s), 4.94 (16β-H, d, J = 4 cps), 3.82 (4-H, s), 3.82 (7-H, s).

Anal. Calcd for $C_{25}H_{31}ClO_4$: C, 69.63; H, 7.25; Cl, 8.23. Found: C, 69.42; H, 7.35; Cl, 8.24.

B.—A solution of 264 mg of 6-chloro-16α,17α-(dimethylmethylenedioxy)-1,4,6-pregnatriene[8] (9) in 75 ml of ether containing 7.5 mmoles of diazomethane was kept at room temperature for 6 days. After evaporation of the ether, methanol was added to the resulting syrup and a crystalline precipitate of 30 mg, mp 205–210°, λ_{max} 235 mμ (ε 5200) and 293 mμ (ε 16,100), was obtained. The mother liquors were chromatographed on neutral alumina (activity V). The hexane–benzene (1:1) and benzene fractions containing 204 mg of product were combined with the previously obtained crystalline material. Repeated recrystallization gave 25 mg of 6-chloro-16α,17α-(dimethylmethylenedioxy)-1α,2α-(4′,3′,1′-pyrazolino)-4,6-pregnadiene-3,20-dione (10): mp 247–249°; λ_{max} 5.85, 6.02, 6.25, 6.34, 6.49 μ; nmr τ 9.31 (18-H, s), 8.72 (19-H, s), 4.96 (16β-H, br), 4.27 (4-H, s), 3.57 (7-H, m). A satisfactory analysis could not be obtained for this material.

Seventy-five milligrams of crude pyrazoline 10, was treated with 25 ml of acetone containing 0.25 ml of 70% perchloric acid at room temperature for 5 min. The reaction was worked up as described above to give 75 mg of material. Thin layer chromatography on neutral alumina (activity V) using hexane–chloroform (1:4) as the solvent and then elution of the ultraviolet absorbing band with ethyl acetate gave 25 mg of product. Recrystallization from methanol gave 10 mg of 8 which although low

melting (mp 263–265°) had an infrared spectrum identical with that of authentic material and λ_{max} 282 mμ (ε 14,700).

C.—Attempted preparation of **8** by treating 6-chloro-16α,-17α-(dimethylmethylenedioxy)-1,4,6-pregnatriene-3,20-dione[6] (**9**) with dimethylsulfoxonium methylide gave a mixture which even after extensive column and thin layer chromatography could not be resolved.

1α,2α-Methylene-16α,17α-(dimethylmethylenedioxy)-4-pregnene-3,20-dione (16). A.—A solution of 30 mg of 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (**4**) in 5 ml of methanol was added to a hydrogen-saturated suspension of 10 mg of 5% palladium on charcoal in 5 ml of methanol containing 4 mg of potassium hydroxide. The mixture was stirred at room temperature in an atmosphere of hydrogen, and after 1 equiv of hydrogen was absorbed, the catalyst was filtered, the solution was neutralized with glacial acetic acid, and the solvent was evaporated. The residue was dissolved in chloroform, and the chloroform solution was washed with water, dried, and evaporated. Recrystallization of the resulting material from methanol gave 11 mg of 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4-pregnene-3,20-dione (**16**): mp 252–253°; $[\alpha]_D$ +266°; λ_{max} 5.85, 6.03 (br) μ; λ_{max} 240 mμ (ε 12,500); nmr τ 9.33 (18-H, s), 8.71 (19-H, s), 4.97 (16β-H, d, J = 4 cps), 4.46 (4-H, s).

Anal. Calcd for $C_{25}H_{34}O_4$: C, 75.34; H, 8.60. Found: C, 76.37; H, 8.49.

B.—The preparation of **16** by the reaction of 16α,17α-(dimethylmethylenedioxy)-1,4-pregnadiene-3,20-dione[6] (**13**) with a fivefold excess of dimethylsulfoxonium methylide was attempted. Analysis of the crude reaction product by vapor phase chromatography[24] showed that there was 65% starting material and 25% of a material whose retention time was identical with that of **16** in the mixture. The remaining material was present in minor peaks.

1α,2α-Methylene-16α,17α-(dimethylmethylenedioxy)-5β-pregnane-3,20-dione (17).—A solution of 104 mg of 1α,2α-methylene-16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione (**4**) in 20 ml of absolute ethanol containing 200 mg of potassium hydroxide and 25 mg of 10% palladium on charcoal was hydrogenated at room temperature until uptake of hydrogen ceased (3 hr). The solution was filtered, acidified with glacial acetic acid, and evaporated. The residue was taken up in ethyl acetate which was washed with saturated salt solution, dried, and evaporated to give 101 mg of material. Two recrystallizations from methanol gave 23 mg of (**17**), mp 182–186°, and no selective absorption in the ultraviolet. The analytical sample had mp 188–190°; $[\alpha]_{589}$ +94°, $[\alpha]_{578}$ +100°, $[\alpha]_{546}$ +179°, $[\alpha]_{436}$ +214°, $[\alpha]_{365}$ +442°; ORD[28] (methanol) $[\alpha]_{350}$ +531°, $[\alpha]_{325}$ +1460°, $[\alpha]_{307}$ ±0°, $[\alpha]_{290}$ −2130° (trough), $[\alpha]_{268}$ ±0°, $[\alpha]_{260}$ +850°; λ_{max} 5.84 (sh), 5.89 μ; nmr τ 9.37 (18-H, s), 8.75 (19-H, s), 4.99 (16β-H, d, J = 4.5 cps).

Anal. Calcd for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06. Found: C, 74.83; H, 9.04.

6α,7α-Methylene-16α,17α-(dimethylmethylenedioxy)-4-pregnene-3,20-dione (15).—A solution of 387 mg of 16α,17α-(dimethylmethylenedioxy)-4,6-pregnadiene-3,20-dione[6] (**14**) in 25 ml of dimethyl sulfoxide containing 5 mmoles of dimethylsulfoxonium methylide was stirred for 23 hr. After work-up as described above 364 mg of an oil was obtained. Thin layer chromatography (neutral alumina, activity V) using hexane–chloroform (1:4) as the developing solvent and eluting the ultraviolet absorbing band with ethyl acetate gave 284 mg of crystalline material. Recrystallization from methanol afforded 69 mg of **15**, mp 200–203°. The analytical sample had mp 207–209°; $[\alpha]_D$ −83°; λ_{max} 5.85, 6.0 (br), 6.26 μ; λ_{max} 267 mμ (ε 16,600); nmr τ 9.38 (18-H, s), 8.91 (19-H, s), 4.97 (16β-H, br), 4.00 (4-H, s).

Anal. Calcd for $C_{25}H_{34}O_4$: C, 75.34; H, 8.60. Found: C, 75.45; H, 8.63.

4β,5-Methylene-16α,17α-(dimethylmethylenedioxy)-19-nor-5β-pregnane-3,20-dione (12).—Dimethylsulfoxonium methylide (2.5 mmoles) and 187 mg of 16α,17α-(dimethylmethylenedioxy)-19-nor-4-pregnene-3,20-dione[19] (**11b**) in 6 ml of dimethyl sulfoxide were stirred for 17.5 hr. After work-up, 158 mg of material having no selective absorption in the 220–250-mμ region was obtained. This material was purified by thin layer chromatography on neutral alumina (activity V) using hexane–chloroform (1:4) as the solvent. Elution of the iodine-absorbing band with ethyl acetate gave 95 mg of 4β,5-methylene-16α,17α-(dimethylmethylenedioxy)-19-nor-5β-pregnane-3,20-dione (**12**). Recrystallization from methanol afforded analytically pure material having mp 155–157°; $[\alpha]_{589}$ +81°, $[\alpha]_{578}$ +84°, $[\alpha]_{546}$ +101°, $[\alpha]_{436}$ +228°, $[\alpha]_{365}$ +600°; ORD[28] (methanol) $[\alpha]_{350}$ +1090°, $[\alpha]_{318}$ +2471° (peak) $[\alpha]_{257}$ ±0°, $[\alpha]_{270}$ −3420°; λ_{max} 5.85, 5.95 μ; nmr τ 9.38 (18-H, s), 4.99 (16β-H, d, J = 4 cps).

Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.50; H, 8.89.

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The Isonitrile–Nitrile Isomerization[1]

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The unimolecular first-order thermal isomerization of isonitriles to nitriles has been investigated in a series of aryl- and alkylisonitriles. Retention of stereochemical integrity at the migrating carbon atom, lack of carbon skeleton rearrangement in the isomerization of cyclobutylisonitrile, and low sensitivity of the reaction rate to variation in *para* substituents in arylisonitriles, all support the view that bond breaking and bond making are essentially synchronous, and that little charge separation develops in the transition state.

The thermal isomerization of isonitriles to nitriles (eq 1) has been known for more than 50 years,[3]

$$R-\overset{+}{N}\equiv\overset{-}{C}: \xrightarrow{\Delta} :N\equiv C-R \qquad (1)$$

but until recently[4] has received scant attention,[5] despite the stoichiometric simplicity of the transformation, and the striking parallel between geometry and bonding in the initial and final states. Rabinovitch and his co-workers have carefully examined the kinetic behavior of *p*-tolylisonitrile[4a] in solution and in

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(3) H. Guillemard, *Compt. Rend.*, **144**, 141 (1907).

(4) (a) G. Kohlmaier and B. S. Rabinovitch, *J. Phys. Chem.*, **63**, 1793 (1959); (b) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962); (c) F. W. Schneider and B. S. Rabinovitch, *ibid.*, **85**, 2365 (1963).

(5) R. A. Ogg, Jr., *J. Chem. Phys.*, **7**, 753 (1939).