the halogenation reaction in eight solvent systems are in excellent agreement, Table V. Thus, the Baker–Nathan order is maintained quantitatively in these eight media covering a span of absolute reactivity of 10^4 with major variation in reagent selectivity and large structural modifications in the solvent.

Unfortunately, side-reactions have prevented the evaluation of the partial rate factors for the non-catalytic chlorination reaction in nitrobenzene, acetic anhydride and chlorobenzene. In these solvents, the relative rate, $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$ is approximately 2 in accord with the observations for the other media. These results are qualitative in the sense that ρ cannot be eliminated from consideration. Nevertheless, the conclusion appears clear that the alkyl groups are responding to the electron-deficiency in the same fashion in all these solvents.

In summary, the relative rate for the chlorination of toluene extends over a range of more than 10^5 from dry chlorobenzene to highly aqueous acetic acid. This large variation in rate does not give rise to significant alteration of the Baker–Nathan order for *p*-substitution in toluene and *t*-butylbenzene. The quantitative evaluation of the greatly modified partial rate factors for reaction in non-aqueous nonhydroxylic solvents provides evidence for the independence of the influence of the alkyl groups from the selectivity of the reagent. Further, the structural, dielectric and solvation properties of the reaction media have been varied over a wide range without apparent modification of the contributions of the electric influences of the *p*-methyl and *p*-*t*-butyl groups. The results of this study and our earlier report support the view that the Baker–Nathan effect is to be identified with a polar influence.

Experimental Part

Materials.—The source of the aromatic materials have been presented previously.[5] The solvents under examination here were obtained in the highest state of purity available commercially and further purified by treatment with chlorine and other conventional methods prior to fractionation. The boiling point and other physical properties were in agreement with literature values. The dark rate of reaction with chlorine was adopted as the principal criterion of purity. As discussed in the Results, acetic anhydride exhibited a significant rate of consumption of chlorine, $k_1 = 2.6 \times 10^{-5}$ sec.$^{-1}$. For the other solvents this reaction was not important in the absence of added hydrogen chloride.

Kinetic Observations.—The kinetic results were obtained as described.[5,7]

Product Distributions.—The methods employed for the analysis of the products have been described.[5] All reactions were carried out in the dark to avoid initiation of radical reactions. Large aromatic to chlorine ratios, 10 to 1.0 or greater, avoided disubstitution as checked by vapor phase chromatography. A curious result was obtained for chlorination in chlorobenzene in preliminary experiments. It was observed that the mixing of two homogeneous solutions of aromatic and chlorine in chlorobenzene led to another homogeneous solution which became opaque after a brief interval. The products of chlorination of a large excess of *t*-butylbenzene in such a solution were about 50% monochloro- and 50% dichloro-*t*-butylbenzene. The principal product was identified as 3,4-dichloro-*t*-butylbenzene by the infrared spectrum[19] of material trapped from the chromatography column. The opaque solution was shown to be the result of hydrogen chloride in moist chlorobenzene. Careful drying of the solvent obviated the problem. The product acid apparently caused a phase separation of traces of water yielding the opaque mixture. The chlorination occurred rapidly in the aqueous phase and the reaction presumably was controlled by the slow rate of transfer across the phase boundary with disubstituted material resulting from the chlorination of the trapped monochloro compound.

Acknowledgment.—It is a pleasure to acknowledge the support of the Research Corporation.

(19) M. Lerer, C. Fabre and G. Hugel, *Bull. soc. chim.*, 177 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY, STANFORD, CALIF.]

Optical Rotatory Dispersion Studies. LIX.[1] The Octant Rule and Deuterium. Synthesis of 3-Deuteriocyclopentanone[2]

BY CARL DJERASSI AND B. TURSCH

RECEIVED JULY 7, 1961

In order to examine the rotational contribution of a deuterium atom β to a carbonyl group, a stereospecific synthesis of 3-deuteriocyclopentanone (XI) was developed starting with (+)-α-pinene (IV).

A substantial amount of work has been done in recent years[3] on optically active substances of type R_1R_2CHD, the deuterium atom representing one of the substituents attached directly to the asymmetric carbon atom. Such compounds have proved to possess very low rotations and it seemed to us of interest to determine whether a situation could be found where "asymmetric deuterium" might produce a large rotational contribution. A valuable test case would be an optically active cyclic ketone, where the rotational effect of a suitably placed deuterium substituent could be examined in the ultraviolet near the extremum of the Cotton effect associated with the carbonyl group.[4] In terms of the tenets of the octant rule,[5] what we would be attempting to measure is the interaction between the electrons in the excited-state orbitals of the carbonyl's n $\rightarrow$ π^*-transition

(1) Paper LVIII, C. Djerassi, P. Quitt, E. Mosettig, R. C. Cambie, P. S. Rutledge and L. H. Briggs, *J. Am. Chem. Soc.*, **83**, 3720 (1961).

(2) Supported by grant No. CRTY-5061 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(3) For pertinent references see A. Streitwieser, Jr., J. R. Wolfe and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959).

(4) See C. Djerassi, "Optical Rotatory Dispersion," McGraw–Hill Book Co., Inc., New York, N. Y., 1960.

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

and the partially unshielded nucleus of the deuterium atom.

As a first example, there was measured the rotatory dispersion curve of 3β-acetoxy-6β-deuteriocholestan-7-one (I),[6] but the amplitude of its Cotton effect was identical with that[7] of 3β-acetoxycholestan-7-one (II), thus implying that an axially oriented deuterium atom adjacent to the carbonyl group of a cyclohexanone exerts only a negligible contribution.

In spite of this result, we felt that a second test case should be examined, where the only asymmetric substituent is the deuterium atom; for this purpose we selected 3-deuteriocyclopentanone (XI). It has been noted earlier[8] that the amplitude of the Cotton effect of (+)-3-methylcyclopentanone (III) was five times larger than that of (+)-3-methylcyclohexanone, this increase probably being due[9] to the asymmetric nature of the C-3 ring carbon in the cyclopentanone, in contrast to the symmetrical cyclohexanone ring, where the principal rotational contribution presumably comes from the extranuclear methyl substituent. As the molecular amplitude of the Cotton effect of (+)-3-methylcyclopentanone (III)[8] exceeds 8700°, it would be a simple matter to recognize a rotational contribution by "asymmetric deuterium" even if its effect were only one-hundredth that of the methyl group.

Turning now to the problem of preparing the substrate for such measurements, it was clear that a method of synthesis had to be devised which did not involve a resolution step after the introduction of the deuterium substituent. This prerequisite was indispensable, as otherwise it would have been impossible to decide with certainty upon a possible negligible rotational contribution by deuterium, which might have been due to incomplete resolution.

The starting material in our synthesis was (+)-α-pinene (IV) whose absolute configuration is known.[10] Oxidation to pinonic acid (V)[11] and pyrolysis[12] of its calcium salt provided (−)-3-isopropenylcyclopentanone (VI). It is pertinent to point out that the latter's negative Cotton effect, when contrasted with the positive one[8] of (+)-3-methylcyclopentanone (III) of established absolute stereochemistry,[13] would have yielded an absolute configurational assignment for (+)-α-pinene (IV) by rotatory dispersion means,[14] if a chemical proof[10] had not already been available. Lithium aluminum hydride reduction of the ketone VI led to a mixture of *cis*- and *trans*-alcohols (VIIa, VIIIa), which were not separable by gas phase chromatography. As the homogeneity of this alcohol was of crucial importance for our subsequent argument, attempts were made to convert the alcohols into crystalline derivatives, which would be separable by crystallization or column chromatography. No success was met with the tosylate, brosylate, 3,5-dinitrobenzoate, *p*-nitrobenzoate, hydrogen phthalate or benzoate derivatives, but treatment with the acid chloride of Δ⁵-3β-acetoxyetienic acid[15] furnished a crystalline etienate mixture (VIIb, VIIIb), which could be resolved into its pure components by fractional crystallization. Using optical rotation as the criterion, one can calculate that the crude lithium aluminum hydride product consisted of 80% of one alcohol and 20% of its epimer. On the assumption that the double bond plays no role and that the reducing agent enters preferentially from the less hindered side, the predominant isomer (used for the subsequent steps) is assigned the *cis* stereochemistry (VIIa).[16] The pure alcohol VIIa regenerated from the pure etienate VIIb now afforded a crystalline tosylate VIIc, which was rather unstable and, therefore, was reduced immediately with lithium aluminum deuteride[17] to *trans*-1-isopropenyl-3-deuteriocyclopentane (IX). Initially it was planned to transform the isopropenyl grouping into an acetyl substituent, which could then be converted into a carbonyl group by Baeyer–Villiger oxidation, saponification and oxidation. However, model experiments with isopropenylcyclopentane coupled with infrared spectral monitoring, showed that acid treatment resulted in nearly complete disappearance of the terminal double bond with formation of some isopropylidenecyclopentane, whose presence was demonstrated by ozonolysis to cyclopentanone. While proceeding in poor over-all yield, this sequence was selected because of its rapidity and pure 1-isopropenyl-3-deuteriocyclopentane (IX) was heated with naphthalenesulfonic acid for 2 hr. The resulting mixture containing 1-isopropylidenecyclopentane (X) was not purified but was ozonized directly and 3-deuteriocyclopentanone (XI) was isolated by gas phase chromatography. The substance had the correct infrared carbonyl band for a cyclopentanone and, most importantly, its mass spectrum[18] exhibited a strong molecular ion peak of mass 85, which is only consistent with structure XI.

The above sequence of reactions must have yielded 3-deuteriocyclopentanone (XI) of at least 80% optical purity.[17] Rotatory dispersion measurement of this product in isoöctane solution yielded no noticeable rotation at 322 mμ under conditions where $[\alpha]_{322}$ 42° would have been detected. Since (+)-3-methylcyclopentanone (III) exhibits a specific rotation of over 4000° at that wave length, one can conclude that, insofar as

(6) E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **78**, 6269 (1956). We are indebted to Prof. Corey for a specimen of I.

(7) C. Djerassi, W. Closson and A. E. Lippman, *ibid.*, **78**, 3163 (1956).

(8) C. Djerassi and G. W. Krakower, *ibid.*, **81**, 237 (1959).

(9) W. Klyne, *Bull. soc. chim. France*, 1397 (1960).

(10) See A. J. Birch, *Ann. Repts. Progr. Chem.*, **47**, 191 (1950).

(11) See M. Delepine, *Bull. soc. chim. France*, 1369 (1936), and earlier references.

(12) Y. R. Naves, *ibid.*, 1372 (1958); see also M. Harispe, A. Boime and R. Charonnat, *ibid.*, 481 (1958).

(13) See E. J. Eisenbraun and S. M. McElvain, *J. Am. Chem. Soc.*, **77**, 3383 (1955).

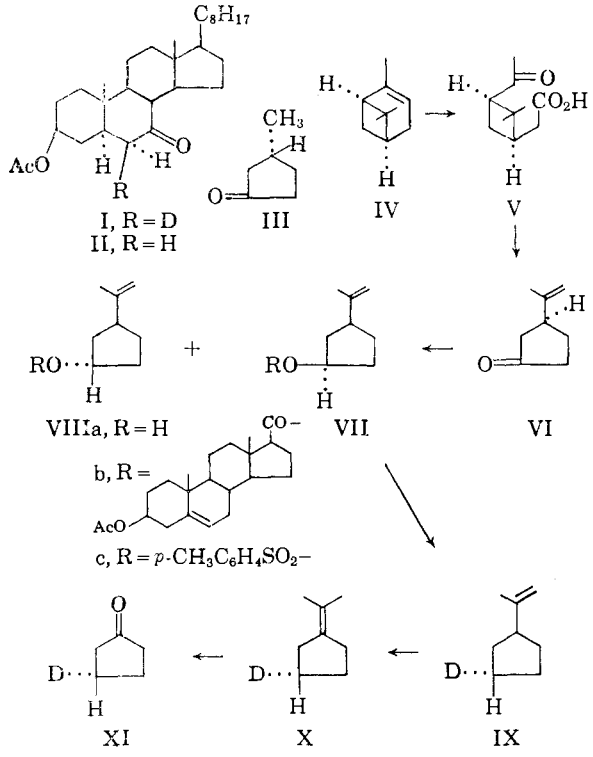
(14) The only assumption made is that the effect of a methyl and isopropenyl group can be equated qualitatively, which we know to be valid from experiments in the cyclohexanone series (J. Osiecki, Ph.D. thesis, Stanford University, 1960).

(15) See C. Djerassi and J. Staunton, *J. Am. Chem. Soc.*, **83**, 736 (1961), for an improved synthesis of this acid.

(16) The actual assignment of configuration is not of any consequence as far as determining the rotational effect of deuterium in optically active 3-deuteriocyclopentanone is concerned, the only important factor being stereochemical homogeneity.

(17) G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, **22**, 479 (1957), demonstrated that such reduction of a secondary sulfonate ester proceeds with inversion to the extent of a least 80%.

(18) We are indebted to Dr. Herbert Budzikiewicz of this Laboratory for the mass spectral determination.



octant rule[5] contributions are concerned, deuterium exhibits at best one-hundredth the rotational effect of methyl.

Experimental[19]

(−)-3-Isopropenylcyclopentanone (VI).[12]—The oxidation of 68 g. of (+)-α-pinene (IV)[20] with potassium permanganate was conducted according to the literature[11] and afforded 28 g. of pinonic acid (V), m.p. 67.5–69°, $[\alpha]^{26}D$ +89° (*c* 1.3), which was transformed into its calcium salt with calcium carbonate in methanol–water. Pyrolysis of the dried (40° (1 mm.)) calcium salt was conducted in a stream of carbon dioxide at an inside temperature of 320° and the distillate was extracted with ether, washed, dried, the solvent evaporated and the residue fractionated to afford 26% of pale yellow (−)-3-isopropenylcyclopentanone (VI), b.p. 70–75° (10 mm.). In order to obtain colorless material, the ketone was converted (semicarbazide hydrochloride, sodium acetate, ethanol, 2 hr., room temperature) in 97% yield into the semicarbazone, m.p. 174–175° (from ethanol) $[\alpha]D$ −28.2° (*c* 0.8) and then regenerated (shaking at room temperature with ether–5% aq. hydrochloric acid) in 78% yield. The colorless ketone exhibited b.p. 70° (10 mm.), $[\alpha]D$ −110.3° (*c* 1.44), and appeared to be at least 98% pure by gas phase chromatography at 100° on a Craig succinate column. The infrared spectrum corresponded in all details to that reported by Naves.[12]

R.D. in isoöctane (*c* 0.12): $[\alpha]_{589}$ −98°, $[\alpha]_{320}$ −3010°, $[\alpha]_{315}$ −2200°, $[\alpha]_{310}$ −3550°, $[\alpha]_{304}$ −328°, $[\alpha]_{300}$ −1020°, $[\alpha]_{290}$ +1800° (shoulder), $[\alpha]_{275}$ +3410°, $[\alpha]_{260}$ +2900°; R.D. in *methanol* (*c* 0.12): $[\alpha]_{589}$ −84°, $[\alpha]_{315}$ −2940° (infl.), $[\alpha]_{310}$ −3340°, $[\alpha]_{267}$ +4000°, $[\alpha]_{250}$ +3200°.

Lithium Aluminum Hydride Reduction of (−)-3-Isopropenylcyclopentanone (VI) and Separation of Isomers (VIIa, VIIIa).—The reduction of 1.03 g. of pure VI (regenerated from semicarbazone) was performed in ether solution by heating under reflux for 30 min. with 0.26 g. of lithium aluminum hydride followed by decomposition with water. The pleasantly smelling alcohol (VIIa, VIIIa) exhibited b.p. 70° (6 mm.), $[\alpha]D$ +8.1° (*c* 1.28), λ_{max} 2.94, 6.15, 9.35 and 11.30 μ.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14: H, 11.18. Found: C, 76.28: H, 10.92.

Gas phase chromatography of the alcohol or acetate on a Craig succinate column showed only one peak, but attempts to obtain a crystalline tosylate, brosylate, benzoate, dinitrobenzoate, *p*-nitrobenzoate or phthalate failed. The inhomogeneous nature of the reduction product was finally demonstrated through the 3β-acetoxyetienates VIIb and VIIIb as follows:

Δ^5-3β-Acetoxyetienic acid[15] (57 g.) in 500 cc. of dry benzene was left overnight with 100 g. of oxalyl chloride and then evaporated to dryness. The acid chloride was suspended in 500 cc. of pyridine, 10.7 g. of the lithium aluminum hydride reduction product was added, the mixture left at room temperature for 20 hr. and then poured into ice and hydrochloric acid. The precipitate was collected, extracted with ether and the latter combined with an ether extract of the filtrate. The ether solutions were filtered through neutral alumina (activity II) and the solvent was evaporated to afford 36.0 g. of a mixture of etienates (VIIb, VIIIb) as a light yellowish solid, m.p. 70–100°, $[\alpha]D$ −30.2° (*c* 10.0); λ_{max} 5.78, 6.15, 8.05 and 11.20 μ. This mixture exhibited only one spot in a thin layer chromatogram (silica gel with 1% ethyl acetate in benzene) and could not be resolved by column chromatography (all eluates exhibited $[\alpha]D$ −30°). Five fractional recrystallizations from methanol (90%)–dioxane (5%)–acetonitrile (5%) by the triangular scheme—each precipitate and filtrate being monitored by optical rotation—afforded in the less soluble fraction 24.9 g. of the etienate VIIb of *cis*-3-isopropenylcyclopentanol,[18] m.p. 120–121°, $[\alpha]D$ −34.2°.

Anal. Calcd. for $C_{30}H_{44}O_4$: C, 76.88; H, 9.46. Found: C, 76.71; H, 9.21.

The more soluble etienate (VIIIb) showed m.p. 79–82°, $[\alpha]D$ −15.6° (*c* 10.0), and its infrared spectrum was essentially identical with that of VIIb except for slight intensity differences. On the basis of the rotations of the crude etienate mixture and the two pure esters VIIb and VIIIb, the composition of the mixture can be calculated as 79% VIIb and 21% VIIIb.

(+)-cis-3-Isopropenylcyclopentanol (VIIa).—The above etienate ester VIIb (24.3 g., m.p. 120°, $[\alpha]D$ −34°) was cleaved in ether solution with lithium aluminum hydride and the mixture decomposed with sodium sulfate. Most of the steroid diol did not dissolve in ether and the dissolved portion was removed by concentrating the ether solution and adding pentane, whereupon the diol precipitated. Evaporation of the solvent and distillation of the residue at 110° (25 mm.) afforded 5.33 g. of 3-isopropenylcyclopentanol (VIIa), which was used in the next step. The analytical sample was distilled again, b.p. 70–73° (4 mm.), $[\alpha]D$ +5.7° (*c* 1.57); λ_{max} 2.94, 6.13, 9.18 and 11.25 μ.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.88; H, 11.21.

***trans*-1-Isopropenyl-3-deuteriocyclopentane (IX).**—A mixture of 5.0 g. of the alcohol VIIa, 27 g. of *p*-toluenesulfonyl chloride (freshly recrystallized from hexane) and 220 cc. of dry pyridine was left at room temperature for 36 hr., poured into ice and hydrochloric acid and extracted with ether. The organic extract was washed with hydrochloric acid, water, potassium hydroxide solution, water, dried and filtered through Merck neutral alumina (activity II) to give 10.1 g. of the crystalline tosylate VIIc, m.p. 54–59°. The analytical specimen was obtained by repeated chromatography on alumina and elution with 1% ether in hexane; m.p. 56–59°, $[\alpha]D$ +4.2°; λ_{max} 6.15, 6.33, 7.30, 8.42 and 11.30 μ.

Anal. Calcd. for $C_{15}H_{20}O_3S$: C, 64.27; H, 7.19. Found: C, 64.21; H, 7.09.

The tosylate decomposed on standing and the freshly prepared material (5.0 g.) was immediately reduced in ether solution with lithium aluminum deuteride at room temperature overnight. After decomposition with sodium sulfate, the ether solution was washed well, dried, evaporated and the residue distilled; yield 2.61 g., b.p. 132° (760 mm.), $[\alpha]D$ +0.008° (*c* 23.4), λ_{max} 6.14 and 11.23 μ.

(19) Melting points were determined on the Kofler block. We are grateful to Mr. E. Meier for the microanalyses and to Mrs. Ruth Records for the rotatory dispersion measurements. All optical rotations were measured in chloroform solution while the infrared spectra were obtained as films.

(20) This material possessed $[\alpha]D$ +53.7°, $n^{26}D$ 1.4634, and was kindly donated by Dr. R. A. Bankert of the Naval Stores Research Division, Hercules Powder Co.

Anal. Calcd. for $C_8H_{13}D$: C, 86.40; H, 13.60; mol. wt., 111. Found: C, 85.92; H, 14.47; mol. wt., 111 (by mass spectrometry[18]).

3-Deuteriocyclopentanone (XI).—The double bond isomerization was accomplished by heating on the steam-bath 2.6 g. of the olefin IX with 100 mg. of recrystallized naphthalenesulfonic acid. After 2 hr. the black solution was diluted with 20 cc. of methylene chloride and filtered through neutral alumina (activity II) to afford a light brown solution, whose infrared spectrum indicated the complete disappearance of the terminal olefin bands.

The methylene chloride solution was ozonized at −60° until a blue color persisted, whereupon nitrogen was bubbled through followed by shaking for 2.5 hr. with 20 cc. of 10% potassium hydroxide and 2 cc. of 33% hydrogen peroxide. The colorless organic phase was washed with water, dried over magnesium sulfate and concentrated to a small volume. Purification by gas phase chromatography using a Beckman Megachrom instrument and a Ucon Polar-Chromosorb column at 125° afforded 22 mg. of 3-deuteriocyclopentanone (XI), whose retention time was identical with that of cyclopentanone. The infrared spectrum exhibited a band (carbon tetrachloride) at 5.74 μ and analytical gas chromatography on a phenyldiethanolamine succinate column (100°) indicated a purity in excess of 90%. The mass spectrum[18] showed a strong molecular ion peak at mass 85 as well as the expected fragmentation peaks (by analogy to the mass spectrum[20] of cyclopentanone), such as m/e 56 ($C_4H_6D^+$) and m/e 42 ($C_3H_4D^+$), and indicated a minimum purity of 85% of 3-deuteriocyclopentanone (XI). The rotatory dispersion curve of the ketone was measured in isoöctane solution (c 0.1) and showed no perceptible rotation in the ultraviolet (to 280 mμ) under conditions where with the identical concentration of androstan-17-one a rotation of $[\alpha]_{322}$ +42° would have been measurable.

(20) P. Natalis, *Bull. soc. chim. Belg.*, **67**, 599 (1959); J. H. Beynon, R. A. Saunders and A. E. Williams, *Appl. Spectros.*, **14**, 95 (1960).

[CONTRIBUTION FROM THE ORGANIC CHEMICAL RESEARCH SECTION, LEDERLE LABORATORIES, A DIVISION OF AMERICAN CYANAMID CO., PEARL RIVER, N. Y.]

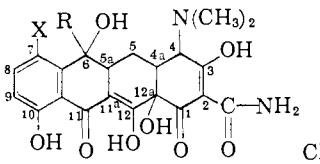
Total Synthesis of Tetracyclines. V. The Stereospecific Elaboration of the Tetracycline Ring System

BY THOMAS L. FIELDS, ANDREW S. KENDE AND JAMES H. BOOTHE

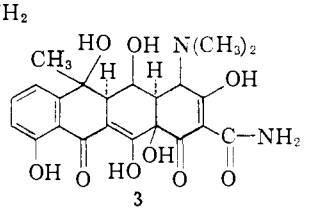
RECEIVED APRIL 28, 1961

The *syn*-(**10**) and *anti*-(**19**) isomers of 5-benzyloxy-8-chloro-1,2,3,4,4a,9,9a,10-octahydro-4,10-dioxo-2-anthraceneacetic acid have been synthesized from the bicyclic intermediate 3-(5-benzyloxy-8-chloro-1,2,3,4-tetrahydro-4-oxo-2-naphthylmethyl)-glutaric acid (**6**). Elaboration of the *syn*-acid **10** into (±)-7-chloro-dedimethylamino-6-demethyl-6,12a-dideoxytetracycline (**17**) and comparison with a sample of **17** obtained by degradation, are described.

One of the more formidable problems associated with the total synthesis of the tetracycline antibiotics arises from the number of asymmetric centers in the molecule.[1] Tetracycline (**1**) itself contains five asymmetric carbon atoms, those numbered 4, 4a, 5a, 6 and 12a. The asymmetric center at 4 is readily epimerized at intermediate *p*H ranges[2] and need not be of early concern in any synthetic scheme. With regard to the angular position C-12a, Holmlund, Andres and Shay[3] have shown that the insertion of the 12a-hydroxyl in the required configuration can be achieved for certain 12a-deoxytetracycline derivatives by gentle oxidative techniques. Furthermore, the catalytic hydrogenolysis of the C-6 hydroxyl group of the 6-demethyltetracyclines[4] does not appreciably affect their antibacterial activity.[5] Therefore, only the asymmetric carbon atoms 4a and 5a are of prime importance in a total synthetic approach to a biologically active tetracycline antibiotic. Since these centers, unlike positions 4 and 12a, are not subject to direct chemical manipulations when part of the intact tetracyclic molecule, their stereoselective formation must be a prerequisite of any successful synthetic scheme.



1, R = CH_3, X = H
2, R = H, X = Cl



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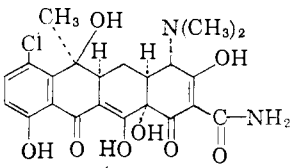

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Although chemical evidence bearing on the stereochemistry of positions 4a and 5a is scanty, Woodward, *et al.*,[6] have suggested that the highly enolic character of 5-hydroxytetracycline (**3**) and its derivatives points toward a *syn* relationship.

(1) For a more complete discussion of the problems involved in the synthetic work see the previous paper in this series: A. S. Kende, T. L. Fields, J. H. Boothe and S. Kushner, *J. Am. Chem. Soc.*, **83**, 439 (1961).

(2) (a) A. P. Doerschuk, B. A. Bittler and J. R. D. McCormick, *ibid.*, **77**, 4687 (1955); (b) C. R. Stephens, L. H. Conover, P. N. Gordon, F. C. Pennington, R. L. Wagner, K. J. Brunings and F. J. Pilgrim, *ibid.*, **78**, 1515 (1956); (c) J. R. D. McCormick, S. M. Fox, L. L. Smith, B. A. Bittler, J. Reichenthal, V. E. Origoni, W. H. Muller, R. Winterbottom and A. P. Doerschuk, *ibid.*, **78**, 3547 (1956); (d) J. R. D. McCormick, S. M. Fox, L. L. Smith, B. A. Bittler, J. Reichenthal, V. E. Origoni, W. H. Muller, R. Winterbottom and A. P. Doerschuk, *ibid.*, **79**, 2849 (1957).

(3) C. E. Holmlund, W. W. Andres and A. J. Shay, *ibid.*, **81**, 4748 (1959).

(4) (a) J. R. D. McCormick, N. O. Sjolander, U. Hirsch, E. R. Jensen, A. P. Doerschuk, *ibid.*, **79**, 4561 (1957); (b) J. S. Webb, R. W. Broschard, D. B. Cosulich, W. J. Stein and C. F. Wolf, *ibid.*, **79**, 4563 (1957); (c) J. H. Boothe, A. Green, J. P. Petisi, R. G. Wilkinson and C. W. Waller, *ibid.*, **79**, 4564 (1957).

(5) J. R. D. McCormick, E. R. Jensen, P. A. Miller and A. P. Doerschuk, *ibid.*, **82**, 3381 (1960).

(6) F. A. Hochstein, C. R. Stephens, L. H. Conover, P. P. Regna, R. Pasternack, P. N. Gordon, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *ibid.*, **75**, 5455 (1953).