Tetrahedron, 1961, Vol. 12, pp. 196 to 204. Pergamon Press, Inc. Printed in Northern Ireland

STUDIES IN STEREOCHEMISTRY—I

STEREOSPECIFIC ROUTES TO *TRANS- ANTI-* AND *CIS-SYN*-Δ^8-DODECAHYDROPHENANTHRENES

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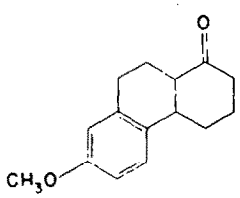
(*Received* 15 *August* 1960)

Abstract—Reduction of *trans*-1-oxo-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (XI) by lithium tri-t-butoxyaluminohydride gave *trans*-1β-hydroxy-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (XII) which on lithium–liquid ammonia reduction gave *trans-anti*-1β-hydroxy-7-oxo-$\Delta^{8(14)}$-dodecahydrophenanthrene (XIII). Reduction of *cis*-1-oxo-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (XV) by sodium borohydride gave *cis*-1α-hydroxy-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (XVI) which on lithium–liquid ammonia reduction gave *cis-syn*-1α-hydroxy-7-oxo-$\Delta^{8(14)}$-dodecahydrophenanthrene (XVII).

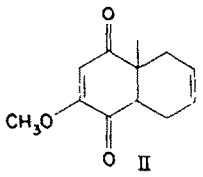
THE method of conformational analysis[1] has been employed with considerable success to the problem of the differences in the thermodynamic stabilities of stereoisomers in polycyclic systems. Thus the greater stability of *trans*- over *cis*-decalin is well-rationalized,[2] as also the stability orders in the perhydrophenanthrene and hydrindane series.[3,4] The introduction of functional groups like the ketogroup into the saturated systems, however, modifies the relative stabilities of the stereoisomers.[5] The conformational alterations introduced by double bonds are less easily understood and have recently been the subject of interesting speculation.[6–9] Some of the experimentally observed deviations in stability order are given below. The *cis*- and *trans*-forms of the octahydrophenanthrone (I), which is conformationally equivalent to an octalone, are present in the ratio of 1:4 in the equilibrium mixture,[10] in contrast to the case of the decalones, where the equilibrium is entirely in favour of the *trans*-isomer. A more complicated example is the diketone (II), the *cis*- and *trans*-forms of which are of the same order of stability.[11] The metal–alcohol reduction of the central double bond of the tetrahydrochrysene derivative (III) yields nearly equal amounts of the *cis*- and *trans*-forms of the corresponding hexahydrochrysene.[12,13] Since carbanion reductions proceed with predominant thermodynamic control,[14] this could be taken as evidence that the two stereoisomers are of equal stability. Recently Wenkert and

[1] D. H. R. Barton and R. C. Cookson, *Quart. Rev.* **10**, 44 (1956).
[2] R. B. Turner, *J. Amer. Chem. Soc.* **74**, 2118 (1952).
[3] W. S. Johnson, *Experientia* **7**, 315 (1951); *J. Amer. Chem. Soc.* **75**, 1498 (1953).
[4] G. Quinkert, *Experientia* **13**, 381 (1957).
[5] P. A. Robins and J. Walker, *J. Chem. Soc.* 3960 (1954); 1789 (1955); *Chem. & Ind.* 772 (1955); W. Klyne, *Experientia* **12**, 119 (1956).
[6] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.* **77**, 2505 (1955).
[7] R. B. Turner, W. R. Meador and R. E. Winkler, *J. Amer. Chem. Soc.* **79**, 4122 (1957).
[8] D. A. H. Taylor, *Chem. & Ind.* 250 (1954).
[9] A. S. Dreiding, *Chem. & Ind.* 1419 (1954).
[10] A. J. Birch, H. Smith and R. E. Thornton, *J. Chem. Soc.* 1339 (1957). We are greatly indebted to Prof. A. J. Birch, F.R.S., for encouraging us to undertake the present study.
[11] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *J. Amer. Chem. Soc.* **74**, 4223 (1952).
[12] A. J. Birch and H. Smith, *J. Chem. Soc.* 4909 (1956).
[13] P. A. Robins and J. Walker, *J. Chem. Soc.* 4984 (1957).
[14] D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.* 3045 (1954).

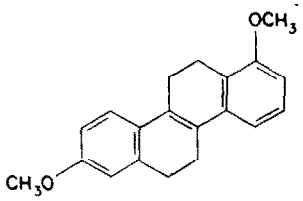
Jackson have made the interesting observation that the ketoesters (IV, V and VI) are highly enolic, whereas the ester (VII) is enolized only to a minor extent.[15] This may be, in part at least, due to the subtle conformational effect of the type noted above.



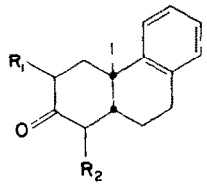
I



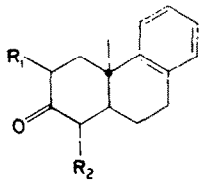
II



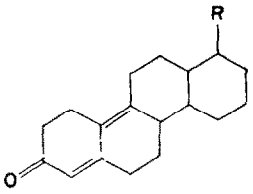
III



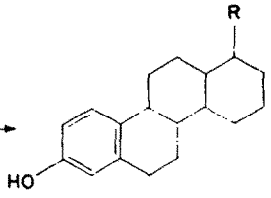
IV $R_1 = CO_2Me$; $R_2 = H$
V $R_1 = H$; $R_2 = CO_2Me$



VI $R_1 = CO_2Me$; $R_2 = H$
VII $R_1 = H$, $R_2 = CO_2Me$



VIII



IX

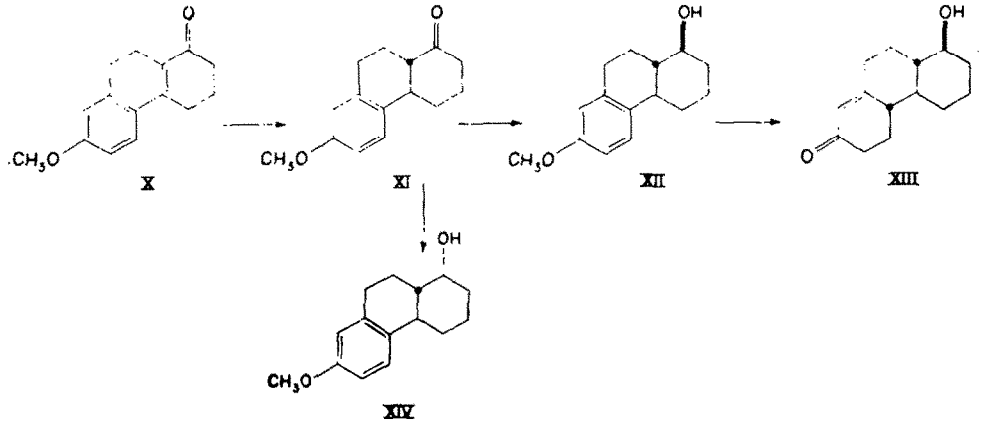
The influence of the double bonds on the relative stabilities of the stereoisomers in the hydrophenanthrene series has not received much attention. The present investigation was started with this aim. It was hoped that the acid-catalysed isomerization of the dienone (VIII) into the phenol (IX) would throw light on the stability orders of the stereoisomers of IX.[16]

The choice of this system was dictated by two reasons: (i) The compounds of type (VIII) were accessible by stereochemically unambiguous routes; (ii) Johnson's work on stereoisomeric oestrones[17] provided ready means of identifying the products.

We report in the present paper, the preparation of two tricyclic intermediates XIII and XVII capable of elaboration to the dienones of type VIII, having the *anti*- and *syn*-backbones respectively. The starting materials for the two series are the *trans*- and *cis*-forms of the octahydrophenanthrone (I), reported by Birch *et al.*[10] by the controlled lithium–ammonia reduction of 1-oxo-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (X).[18]

[15] E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.* **81**, 5601 (1959).
[16] See also: C. Sannie and J. J. Panouse, *Bull. Soc. Chim.* 1435 (1956).
[17] W. S. Johnson, I. A. David, H. C. Dehm, R. J. Highet, E. W. Warnhoff, W. D. Wood and E. T. Jones, *J. Amer. Chem. Soc.* **80**, 661 (1958).
[18] G. Stork, *J. Amer. Chem. Soc.* **69**, 2936 (1947); F. J. Villani, M. S. King and D. Papa, *J. Org. Chem.* **18**, 1578 (1953).

Reduction of *trans*-1-oxo-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (XI) by sodium borohydride gave a mixture of epimeric hydroxy compounds, m.p. 102–103° and 92°, in the ratio 2:1. The major product has been assigned the β-configuration (equatorial-OH) (XII)[19] and the other epimer, the α-configuration (axial-OH) (XIV). The configurations assigned were confirmed as follows:[20] The



compound, m.p. 102°, gave a *p*-nitrobenzoate by treatment with *p*-nitrobenzoyl chloride and pyridine at room temperature, whereas the compound, m.p. 92°, did not react even under vigorous conditions; on chromatography over alumina, the compound, m.p. 92°, was eluted first, by petroleum ether–benzene mixture, and the compound, m.p. 102–103°, later by benzene.

Recently Dauben *et al.*[21] have noted that the borohydride reductions are subject to 'steric approach control' to a greater extent than lithium aluminium hydride reductions. While the result obtained by us is fairly in agreement with this view, the formation of a large amount of the axial epimer (ca. 35%) is somewhat surprising. Probably in this case the 'product development control' factor also operates in favour of the axial epimer to a greater extent than in the cases studied by Dauben *et al.*[21]

We next carried out the reduction of the *trans*-ketone (XI) by lithium tri-t-butoxyaluminohydride,[22] which has been reported to be highly stereospecific.[23,24] By using this method the equatorial hydroxy compound (XII), m.p. 102°, was obtained as the single isolable product in ca. 65 per cent yield. Birch reduction, using the Wilds and Nelson's modification,[25] of XII gave the dihydroderivative in high yield, which on acid hydrolysis gave the *trans-anti*-α,β-unsaturated ketone (XIII). Preparation of the dienone of type VIII, from the unsaturated ketone (XIII) is in progress.

Next we turned to the *syn*-series. So far the *syn*-hydrophenanthrenes were only of

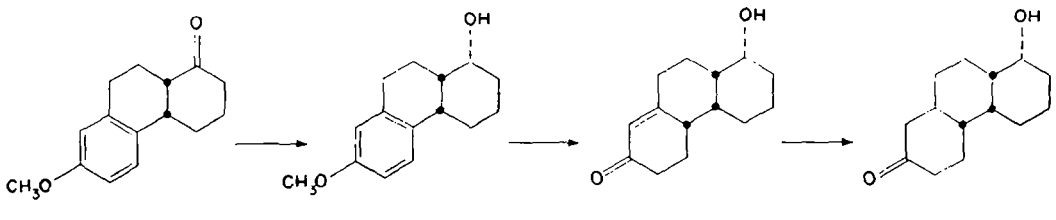
[19] Steroid nomenclature. The hydrogen atom at C_{11} is assumed to be β. The compounds described in this paper are racemic.
[20] D. H. R. Barton, *J. Chem. Soc.* 1027 (1953).
[21] W. G. Dauben, G. J. Fonken and D. S. Noyce, *J. Amer. Chem. Soc.* **78**, 2579 (1956); W. G. Dauben E. J. Blanz, J. Jiu and R. Micheli, *Ibid.* **78**, 3752 (1956).
[22] H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.* **80**, 5372 (1958).
[23] O. H. Wheeler and J. L. Mateos, *Canad. J. Chem.* **36**, 1431 (1958).
[24] J. Fajkos, *Coll. Czech. Chem. Comm.* **24**, 2284 (1959).
[25] A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.* **75**, 5360 (1953).

theoretical interest, but recent work[28–29] has shown that a number of diterpenes have the *syn*-backbone. Presently only two general methods are known for building up such systems. The first takes advantage of the stereospecificity of the Diels–Alder reaction.[30] and the second depends upon the phenomenon of catalyst hindrance observed by Linstead *et al.*[31,32] We have developed a new procedure which makes use of the conformational flexibility of the *cis*-decalin system.[33] The *syn*-compounds prepared by us for the present work are also useful intermediates for the synthesis of diterpenes.

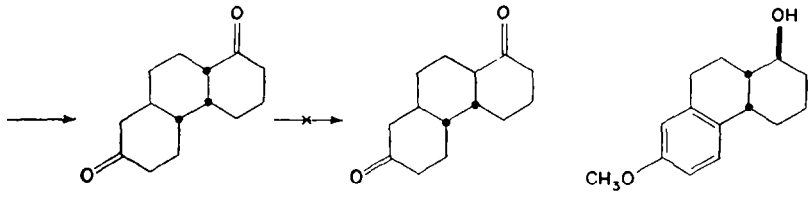
Reduction of *cis*-octahydrophenanthrone (XV)[10] by sodium borohydride gave a single hydroxy compound, which has been assigned the configuration XVI on the following grounds. The *cis*-ketone (XV) could exist in either of the two conformations XXI or XXII and the approach of the reducing hydride species from the concave side of the cage-like structure is highly hindered in both the conformations. Hence XVI appears to be the only reasonable configuration for the reduction product.[34] Reduction of the *cis*-ketone (XV) by lithium tri-t-butoxyaluminohydride was not stereospecific to this extent. Chromatographic separation of the reduction product followed by purification as the *p*-nitrobenzoate showed that the α-hydroxy compound (XVI) was the major product. The other by-product, which must undoubtedly be the epimeric β-hydroxy compound (XXIII) could not be isolated in the pure state. The course of the latter reduction throws some light on the relative stability of the two conformations, XXI and XXII, of the *cis*-ketone (XV). It has been definitely proved by the work of Wheeler and Mateos[23] that the reduction by lithium tri-t-butoxyaluminohydride is subject largely to 'product development control'. With XXII representing the conformation of the *cis*-ketone (XV), the configuration of the reduction product should be (XXIII)[β-OH(e)], whereas the [α-OH(e)] should be derived from the conformation XXI. The isolation of XVI as the major product shows that the *cis*-ketone exists preferentially in the conformation (XXI). This observation is in agreement with the conclusion of Djerassi and Marshall,[35] that *cis*-10-methyl-1-decalone exists preferentially in the conformation XXIV, on the basis of rotatory dispersion measurements.[36]

Next we carried out the lithium–liquid ammonia reduction of the *cis*-1α-hydroxy compound (XVI). The intermediate enol ether (XXV) was isolated in good yield, which on hydrolysis gave the α,β-unsaturated ketone (XVII) in ca. 35 per cent yield together with a considerable amount of the β,γ-unsaturated ketone (XXVI), which could be obtained only in impure condition. The formation of the β,γ-unsaturated ketone is to be attributed to the *cis*-fusion of the C-D rings in XVI. The

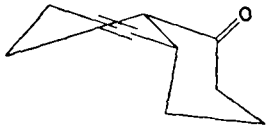
[28] E. Wenkert and J. W. Chamberlin, *J. Amer. Chem. Soc.* **81**, 688 (1959).
[27] O. E. Edwards and R. Howe, *Chem. & Ind.* 537 (1959); *Canad. J. Chem.* **37**, 760 (1959).
[28] B. Green, A. Harris and W. B. Whalley, *J. Chem. Soc.* 4715 (1958).
[29] C. Djerassi, M. Cais and L. A. Mitscher, *J. Amer. Chem. Soc.* **81**, 2387 (1959).
[30] P. A. Robins and J. Walker, *J. Chem. Soc.* 3960 (1954) and later papers in the series.
[31] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. W. Whetstone, *J. Amer. Chem. Soc.* **64**, 1985 (1942) and later papers.
[32a] J. W. Cornforth and R. Robinson, *J. Chem. Soc.* 1855 (1949); [b] W. S. Johnson, J. Ackerman, J. F. Eastham and H. A. DeWalt, Jr., *J. Amer. Chem. Soc.* **78**, 6302 (1956).
[33] For an earlier application of this concept, see R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey and R. W. Kierstead, *Tetrahedron* **2**, 1 (1958).
[34] For an analogy see L. H. Sarett, R. M. Lukes, G. I. Poos, J. M. Robinson, R. E. Beyler, J. M. Vandegrifft and G. E. Arth, *J. Amer. Chem. Soc.* **74**, 1393 (1952); R. E. Beyler and L. H. Sarett, *Ibid.* **74**, 1406 (1952).
[35] C. Djerassi and D. Marshall, *J. Amer. Chem. Soc.* **80**, 3986 (1958).
[36] The referee has kindly pointed out that examination of scale models also shows that XXI is the preferred alternative.



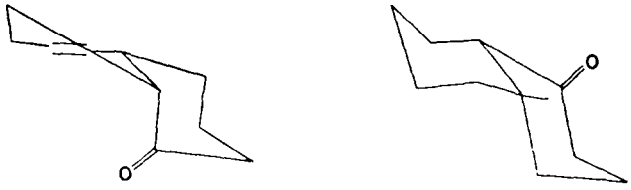
XV XVI XVII XVIII



XIX XX XXIII



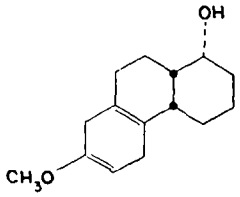
XXI



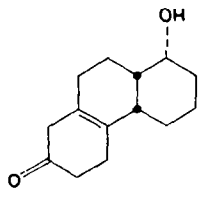
XXII XXIV

configuration XVII, assigned to the α,β-unsaturated ketone is based on the following grounds. The intermediate enol ether (XXV), on hydrolysis, could give rise to the *cis-syn*-unsaturated ketone (XVII) or the corresponding *cis-anti*-isomer (XXVII). It is possible for XVII to exist in an all-chair conformation (XXVIII) in which the hydroxyl group is equatorial. On the other hand two conformations are possible for the *cis-anti*-isomer (XXVII), (XXIXa and b), both of which are energetically unfavourable. The former contains a 1:3-diaxial OH . . . . CH interaction. Conformation XXIXb, having the C-ring in the boat form, is derived from XXIXa by an inversion of the *cis*-decalin part through the intermediacy of XXIXc in which C_5 is axially oriented with respect to ring-C. It should be emphasized that it is not possible to attach ring-B with the α,β-unsaturated ketonic group, if C_5 is axial. Hence ring-C is forced into a boat conformation as in XXIXb. Thus the *cis-syn-configuration* (XVII) appears to be energetically the most favoured one.

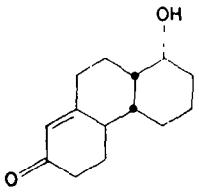
The configuration assigned to the tricyclic ketone (XVII) has been confirmed as follows: Reduction of XVII by lithium–liquid ammonia procedure gave the BCD-*trans-syn-cis* saturated hydroxy ketone (XVIII) which was oxidised by chromium



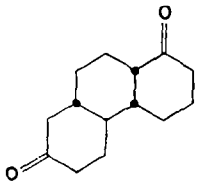
XXV



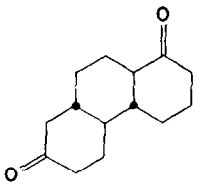
XXVI



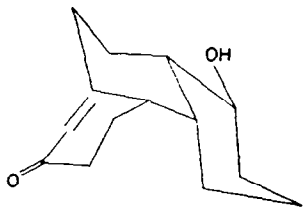
XXVII



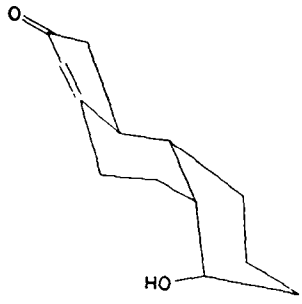
XXX



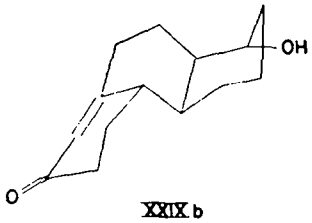
XXXI



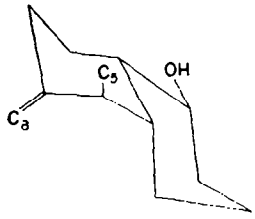
XXVIII



XXIX a



XXIX b



XXIX c

trioxide in pyridine to the *cis-syn-trans*-diketone (XIX). As expected, this did not undergo isomerization on treatment with alkali, because the isomerization product, the *trans-syn-trans*-diketone, is known to be thermodynamically less stable than (XIX).[3] If the unsaturated ketone had the *cis-anti*-configuration (XXVII) the configuration of the derived diketone would be XXX (BCD-*trans-anti-cis*). This would be expected to undergo easy isomerization to the more stable *trans-anti-trans* configuration (XXXI).

Further experiments are in progress to add the A-ring to the enone (XVII) and also to convert it into the isopimaric acid group of diterpenes.

EXPERIMENTAL[37]

trans-anti-Series

Reduction of trans-1-*oxo*-7-*methoxy*-1,2,3,4,9,10,11,12-*octahydrophenanthrene* (xi)

(a) *By sodium borohydride.* To a solution of *trans*-1-oxo-7-methoxy-1,2,3,4,9,10,11,12,-octahydrophenanthrene (XI)[10] (460 mg) in methanol (20 ml) was slowly added a solution of sodium borohydride (380 mg) in water (5 ml). There was a vigorous reaction and after standing for 10 hr at room temp, the mixture was poured into iced dil. HCl. The aqueous solution on standing deposited a white crystalline solid, m.p. 63–68°, yield 280 mg. Separation of this mixture into the epimeric hydroxy compounds XII and XIV was achieved by two methods:

(i) Fractional crystallization from pet ether gave first trans-1β-*hydroxy*-7-*methoxy*-1,2,3,4,9,10,11,12-*octahydrophenanthrene* (XII) as feathery needles, m.p. 102–103°; yield 90 mg; infra-red absorption, 3650 cm^{-1} (OH). (Found: C, 77·52; H, 8·74. $C_{15}H_{20}O_2$ requires: C, 77·59; H, 8·62%).

The mother liquors yielded a solid which on further crystallization from the same solvent furnished colourless stout rods of trans-1α-*hydroxy*-7-*methoxy*-1,2,3,4,9,10,11,12-*octahydrophenanthrene* (XIV), m.p. 92°; yield 30 mg; infra-red absorption, 3675 cm^{-1} (OH). (Found: C, 78·02; H, 8·7. $C_{15}H_{20}O_2$ requires: C, 77·59; H, 8·62%).

(ii) The crude reduction product (170 mg) was chromatographed over Merck's alumina (5 g). Elution with 1:1 pet ether–benzene mixture (40 ml) gave the crude *trans*-1α-hydroxy compound(XIV), m.p. 85–91°; after crystallization it melted at 92°; yield 50 mg. Elution with solvent mixtures containing increasing proportions of benzene gave non-crystalline product (35 mg). Elution with benzene gave the *trans*-1β-hydroxy compound (XII), m.p. 90–100°; after crystallization m.p. 102–103°; yield 75 mg.

p-*Nitrobenzoylation of* XII *and* XIV. A mixture of the equatorial hydroxy compound (XII), m.p. 102–103°, (8·0 mg) and *p*-nitrobenzoyl chloride (8·5 mg) was dissolved in pyridine (2 drops) and left overnight at room temp. The mixture was poured into water and extracted with ether. The extract was washed with dil HCl, water, dil NaOH and water and dried (Na_2SO_4). Removal of the solvent gave 1β-p-*nitrobenzoyloxy*-7-*methoxy*-1,2,3,4,9,10,11,12-*octahydrophenanthrene* (6·1 mg) as fine feathery needles, m.p. 104°, after crystallization from ether–pet ether mixture. Crystallization from benzene–pet ether mixture gave a different polymorph as stout rods, m.p. 148–150°. (Found: N, 3·50. $C_{22}H_{23}O_5N$ requires: N, 3·67%).

The epimeric hydroxy compound (XIV), m.p. 92°, (9·0 mg) on similar treatment was recovered unchanged after a reaction period of 30 hr at room temp. When the reaction was carried out at 80° for 40 min only an oily product was obtained.

(b) *By lithium tri-t-butoxyaluminohydride.* t-Butanol (2·5 ml) was added with stirring to a suspension of lithium aluminium hydride (500 mg) in purified diglyme or tetrahydrofuran (25 ml) maintained below 0° in an ice-salt bath. The *trans*-ketone (XI, 490 mg) in diglyme or tetrahydrofuran was added with stirring to the turbid solution of the hydride at 0°. The mixture was stirred at 0° for 30 min and at room temp for 1 hr. On acidification with iced dil HCl (500 ml), a white precipitate (300 mg) was obtained, m.p. 102–103°, undepressed by admixture with the product XII from the borohydride reduction.

Trans-anti-1β-*Hydroxy*-7-*oxo*-$\Delta^{9(14)}$-*dodecahydrophenanthrene* (XIII). To a stirred solution of lithium (590 mg) in anhydrous liquid ammonia (200 ml) was added a solution of *trans*-1β-hydroxy-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (XII) (325 mg) in anhydrous ether (20 ml). The mixture was stirred for 5 min and anhydrous ethanol (5 ml) was added dropwise during ca 3 min. The solution was stirred till the blue colour disappeared. Ammonia was allowed to evaporate and water was added to the reaction mixture. On letting the mixture stand for 1 hr, a colourless precipitate of trans-1β-*hydroxy*-7-methoxy-1,2,3,4,5,8,9,10,11,12-*decahydrophenanthrene* was obtained; m.p. 124–126°; yield 280 mg. The above dihydro-derivative in the crude state was hydrolysed by refluxing with methanol (14 ml) and 3N HCl (8 ml) under nitrogen for 45 min and then poured onto ice (300 g). The aqueous solution was saturated with $(NH_4)_2SO_4$ and extracted with a mixture of ether and pet ether.

[37] All melting points are uncorrected. U.V. spectra were measured in 95% ethanol. Petroleum ether used in this section had b.p. 40–60°. Microanalyses were carried out by Messrs. B. R. Seetharamia and D. P. Bose of this department.

The extract was washed with brine, ice-cold 2% NaOH solution, brine and a little water and dried (Na_2SO_4). Evaporation of the solvent under vacuum at 30° gave *trans-anti*-1β-hydroxy-7-oxo-$\Delta^{8(14)}$-dodecahydrophenanthrene (XIII), m.p. 140–155°; yield 240 mg. After several crystallizations from ether the product melted at 157–158°. A sample was sublimed for analysis. Infra-red absorption, 3650, 1667, 1613 cm^{-1}; λ_{max} 240 mμ; ε 15,240. (Found: C, 76·03; H, 9·19. $C_{14}H_{20}O_2$ requires: C, 76·36; H, 9·09%).

The 2,4-*dinitrophenylhydrazone* was obtained as a red crystalline powder by Shine's procedure[38] and recrystallized from ethylacetate, m.p. 195–198° (Found: N, 13·72. $C_{20}H_{24}O_5N_4$ requires: N, 13·99%).

The *semicarbazone* was prepared by the sodium acetate procedure, m.p. 246–249° (decomp) after recrystallization from aqueous alcohol. (Found: N, 15·19. $C_{15}H_{23}O_2N_3$ requires: N, 15·15%).

cis-syn-Series

Sodium borohydride reduction of cis-1-*oxo*-7-*methoxy*-1,2,3,4,9,10,11,12-*octahydrophenanthrene* (XV).

The reduction was carried out as described before for the *trans*-compound (XI) using the *cis*-ketone (XV, 110 mg) in methanol (10 ml) and sodium borohydride (200 mg) in water (5 ml). cis-1α-*Hydroxy*-7-*methoxy*-1,2,3,4,9,10,11,12-*octahydrophenanthrene* (XVI) (63·9 mg), m.p. 85–89°, was thus obtained. On recrystallization from ether–pet ether mixture it came out as colourless plates, m.p. 94–96°; mixed m.p. with the *trans*-1α-hydroxycompound (XIV), m.p. 92°, was depressed. In other experiments a different polymorph of (XVI), m.p. 81–83°, was also obtained. The polymorphic relationship was established by melting the lower melting form and seeding it with the higher melting one at 85°, when it resolidified and melted again at 92–96°. Both forms gave the same *p*-nitrobenzoate. A sample was sublimed for analysis at 75° (1 mm). Infra-red absorption, 3680 cm^{-1} (OH). (Found: C, 77·34; H, 8·67. $C_{13}H_{20}O_2$ requires: C, 77·59; H, 8·62%).

The *p*-nitrobenzoate of *cis*-1α-hydroxy-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (XVI) was prepared by the previously described procedure. Crystallization from benzene–pet ether gave fine needles, m.p. 148–150°; mixed m.p. with the *p*-nitrobenzoate of XII was depressed (Found: N, 3·53. $C_{22}H_{23}O_5N$ requires: N, 3·67%).

Lithium tri-t-butoxyaluminohydride reduction of the cis-*ketone* (XV)

Reduction of the *cis*-ketone (XV, 230 mg) in tetrahydrofuran (5 ml) was carried out with lithium tri-t-butoxyaluminohydride prepared from lithium aluminium hydride (210 mg) and t-butanol (1 ml) in tetrahydrofuran (9 ml) by the procedure described above for the *trans* ketone (XI). The oily product, thus obtained, was chromatographed over alumina (6 g). Elution with 3:1 benzene–pet ether mixture gave a low melting product, m.p. ca. 65° (73mg). This gave a *p*-nitrobenzoate (62·0 mg) by the usual procedure, m.p. 115–135°, raised by further crystallization from benzene–pet ether mixture to 148–150°, undepressed by admixture with the *p*-nitrobenzoate of the borohydride reduction product. Elution with ether gave a crystalline solid (75 mg), m.p. 80°, undepressed by admixture with the borohydride reduction product. It gave a *p*-nitrobenzoate, m.p. 145–148°, identical with that reported above.

cis-syn-1α-*Hydroxy*-7-*oxo*-$\Delta^{8(14)}$-*dodecahydrophenanthrene* (XVII)

Reduction of *cis*-1α-hydroxy-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene (XVI, 1·05 g) in ether (25 ml) was carried out with lithium (2·1 g) in anhydrous liquid ammonia (300 ml) and alcohol (17·5 ml) as described before and cis-1α-*hydroxy*-7-*methoxy*-1,2,3,4,5,8,9,10,11,12-*decahydrophenanthrene* (XXV, 950 mg) thus obtained was directly hydrolysed with refluxing methanol (43 ml) and 3N HCl (15 ml) under nitrogen for 20 min. The product was worked up as before and the resulting crude oily product on maceration with ether gave *cis-syn*-1α-hydroxy-7-oxo-$\Delta^{8(14)}$-dodecahydrophenanthrene (XVII, 340 mg), m.p. 136–139°. After recrystallization from ether it melted at 138–140°. A sample was sublimed for analysis at 130° (1 mm). Infra-red absorption: 3704 cm^{-1} (OH); 1664 cm^{-1} (α,β-unsaturated ketone); λ_{max} 241 mμ; ε 17,280 (Found: C, 76·60; H, 9·11. $C_{14}H_{20}O_2$ requires: C, 76·36; H, 9·09%).

The 2,4-*dinitrophenylhydrazone* was obtained as shiny red needles from ethyl acetate, m.p. 181–182° (Found: N, 13·96. $C_{20}H_{24}O_5N_4$ requires: N, 13·99%).

[38] H. J. Shine, *J. Org. Chem.* **24**, 252 (1959).

The mother liquors from the α,β-unsaturated ketone gave a crystalline solid, m.p. 105–125° (150 mg) which showed no absorption maximum in the ultra-violet region. The product, in all probability, is the *β,γ-unsaturated ketone* (XXVI).

cis-syn-trans-1α-*Hydroxy-7-oxo-perhydrophenanthrene* (XVIII)[39]

To a solution of lithium (14·7 mg) in anhydrous liquid ammonia was added a solution of *cis-syn*-1α-hydroxy-7-oxo-$\Delta^{8(14)}$-dodecahydrophenanthrene (XVII), 113 mg) in anhydrous ether and the mixture stirred till the blue colour disappeared. Ice-cold water was cautiously added and the aqeous solution extracted with ether. The extract was washed with water and dried (Na_2SO_4). Removal of solvent gave *cis-syn-trans*-1α-hydroxy-7-oxoperhydrophenanthrene (XVIII, 76·6 mg) m.p. 145–151°, raised to 152–154° after two crystallizations from benzene–pet ether mixture. A sample was sublimed for analysis at 140° (1 mm). Ultra-violet spectrum showed the absence of any α,β-unsaturated ketone $\varepsilon_{286}39$; infra-red absorption 3680 cm^{-1} (OH) and 1701 cm^{-1} (C=O) (Found: C, 75·43; H, 10·02. $C_{14}H_{22}O_2$ requires: C, 75·65; H, 9·91%).

cis-syn-trans-1,7-*Dioxo-perhydrophenanthrene* (XIX)[40]

To the complex of chromium trioxide (127 mg) and pyridine (1·2 ml) was added a solution of *cis-syn-trans*-1α-hydroxy-7-oxo-perhydrophenanthrene (XVII, 70 mg) in pyridine (1·2 ml). The solution, which darkened immediately, was allowed to stand overnight at room temp and then poured into water (150 ml) followed by acidification with 10% H_2SO_4 (50 ml). The aqueous solution was extracted with ether–pet ether mixture. The extract was washed with water, saturated $NaHCO_3$ solution, water and dried (Na_2SO_4). Evaporation of the solvent at room temp under vacuum gave *cis-syn-trans*-1,7-dioxoperhydrophenanthrene (XIX, 35 mg), m.p. 93–98°. After recrystallization from pet ether it melted at 97–98°. Infra-red absorption, 1700 cm^{-1} (C=O) (Found: C, 75·96; H, 9·19. $C_{14}H_{20}O_2$ requires: C, 76·36; H, 9·09%).

Stereochemical stability of cis-syn-trans-1,7-*dioxoperhyrophenanthrene* (XIX)

The diketone (XIX, 9·0 mg), m.p. 97–98°, was refluxed with 2% methanolic KOH (5 ml) under nitrogen for 30 min. The solvent was removed under reduced press and water (25 ml) was added. The aqueous solution was saturated with $(NH_4)_2SO_4$ and extracted with ether–pet ether mixture. The extract was washed with water and dried (Na_2SO_4). Removal of the solent under reduced press and crystallization of the residue from pet ether gave the starting diketone (XIX, 3·0 mg), m.p. 95–98°, either alone or on admixture with starting diketone(XIX), m.p. 97–98°. The low recovery is probably due to some decomposition taking place on alkali treatment.

Acknowledgements—The author is grateful to Professor D. K. Banerjee, D.Sc., F.A.Sc., for kind encouragement and helpful discussions, and to the Council of Scientific & Industrial Research, New Delhi, for financial support.

[39] Procedure of D. K. Banerjee, S. Chatterjee and S. P. Bhattacharyya, *J. Amer. Chem. Soc.* **77**, 404 (1955).
[40] Procedure of G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Amer. Chem. Soc.* **75**, 423 (1953).