Steric Aspects of the Intramolecular Cyclisation of 2-Arylcyclohexylacetic Acids. Part III.¹

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Unambiguous syntheses of *cis*- and *trans*-1,2,3,4,4a,9,10,10a-octahydro-5,8-dimethylphenanthrenes enabled stereochemical assignment for the thermodynamically stable isomer of 1,2,3,4,4a,9,10,10a-octahydro-5,8-dimethyl-4,9-dioxophenanthrene, described recently.¹ Supplementary support was obtained from n.m.r. studies.

STEREOCHEMICAL problems in condensed alicyclic systems have been the subject of numerous studies in recent years.

Our interest in this field derives from the observation ¹ that in contrast to *trans*-2-(3-tolyl)-3-oxocylohexylacetic acid (I), which on cyclisation with hydrogen fluoride yielded only one product,² *trans*-2-(2,5-xylyl)-3-oxocyclohexylacetic acid (II) gave rise to a pair of stereo-isomers of diketone (III). These isomers must differ at the B/c ring junction since it has been found that one



of the isomers can be transformed into the other by sodium methoxide treatment. This epimerisation also

raises the question whether the *cis*- or *trans*-isomer of diketone (III) has the higher thermodynamic stability.

Examination of Dreiding models shows that considerable steric compression would arise from the proximity of the c-ring carbonyl and the 5-CH₃ group only in a B/c trans-fused diketone, but not in a B/c cisfused one. Moreover, it was also predicted that even a B/c trans-fused compound would be free of steric hindrance when methoxyl groups replace the methyls. Synthesis of trans-2-(2,5-dimethoxyphenyl)cyclohexylacetic acid and subsequent hydrogen fluoride cyclisation proved this assumption to be correct.¹ These considerations suggested higher thermodynamic stability for the B/c cis-fused isomer of compound (III) and this view has now been confirmed by chemical transformations and by n.m.r. studies.

Chemical structure proof was achieved by unambiguous

¹ Part II, S. Bien, L. Cohen, and K. Scheinmann, J. Chem. Soc., 1965, 1495.

² S. Bien and M. Boazi, J. Chem. Soc., 1959, 1727.

J. Chem. Soc. (C), 1967

synthesis of the two stereoisomeric cis- and transoctahydrophenanthrenes (VIII) and (XI) and comparison of these with the hydrocarbon obtained by complete reduction of the stable epimer of diketone (III).

The authentic hydrocarbons (VIII) and (XI) have been obtained by ring closure of the corresponding acids (VI) and (IX), where the absence of the keto-group at C-4 eliminates any possibility of epimerisation either during the cyclisation step or in the work-up. The trans-acid (IX) was readily available by Wolff-Kishner reduction of the keto-acid (II). The corresponding cisisomer was synthesised through the unsaturated dinitrile (V), obtained from 2-(2,5-xylyl)cyclohexanone (IV) and malononitrile by a Knoevenagel-type condensation successfully used for the synthesis of ylidenemalononitriles.³⁻⁵

Acid hydrolysis of the unsaturated dinitrile (V) afforded an oily acidic product characterised by its S-benzylthiouronium salt. Analytical data were in 1H) and the C-2 proton (centred at $\delta 4.00$ p.p.m., 1H). Similarly, the benzylic proton at C-2 in the unsaturated dinitrile (V) appeared at δ 4.17 p.p.m.

Also, whereas the acid (XIII) showed λ_{max} 218 mµ, which is characteristic of alicyclic α,β -unsaturated acids,⁶ its isomer (XII) showed maximum absorption at 240 mµ indicating the presence of a styrene chromophore. The low intensity of the latter band (c 2200; cf. 1-phenylcyclohexene, λ_{max} 248 mµ, ϵ 10,000) may be attributed to inhibition by the 2-methyl group of complete coplanarity of the double bond and the aromatic ring.^{7,8} Since hydrogenation of the acid (XII) afforded a mixture of cis- and trans- acids (VI) and (IX), this projected route was abandoned.

An alternative approach was based on earlier observations 3,9,10 showing that the double bond of α,β -unsaturated nitriles undergoes catalytic reduction selectively before the nitrile group. In accordance with this finding 2-(2,5-xylyl)cyclohexylidenemalononitrile (V) on



Reagents: I, HCI-AcOH; 2, H₂Pt-C, HCI-AcOH; 3, HF; 4, Wolff-Kishner; 5, CH₂(CN)₂; 6, NaOMe, Wolff-Kishner; 7, Wittig; 8, H₂-Pd-AcOH; 9, NaOMe-MeOH

accordance with an unsaturated acid, but no n.m.r. signal was found in the vinyl proton region. A signal equivalent to two hydrogens at 8 2.80 p.p.m. $(-C=C\cdot CH_{2}\cdot CO_{2}H)$ indicated that a double bond shift during the hydrolysis had led to the β_{γ} -unsaturated acid (XII). This view was supported by n.m.r. spectral data for the authentic isomeric acid (XIII),* which exhibited signals for both a vinyl proton (δ 4.95 p.p.m.,

* Preparation of this acid from 2-(2,5-xylyl)cyclohexanone, by a Wittig-type reaction, will be described in a forthcoming publication

- ³ J. G. Murphy, J. Org. Chem., 1961, 26, 3104.
- ⁴ D. T. Mowry, J. Amer. Chem. Soc., 1945, **67**, 1050.
 ⁵ E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and D. R. Maulding, J. Org. Chem., 1962, **27**, 4428.

 - ⁶ A. T. Nielsen, J. Org. Chem., 1957, 22, 1539.

hydrogenation yielded a saturated nitrile which, without further purification, was hydrolysed and decarboxylated to the desired *cis*-acid (VI) as a single product. Scale molecular models (Fischer-Taylor-Hirschfelder) of the unsaturated dinitrile showed that double bond-catalyst interaction is highly favoured from the remote side of the p-xylyl group, thus predicting preferential formation of the *cis*-acid (VI), as observed experimentally.

- 7 R. B. Carlin and H. P. Landerl, J. Amer. Chem. Soc., 1953, 75, 3969.
- ⁸ E. K. Weisburger and J. H. Weisburger, J. Org. Chem., 1958,
- 23, 1193.
 ⁹ Houben-Weyl, "Methoden der Organischen Chemie," Georg Thieme Verlag, Stuttgart, 1957, vol. XI/1, p. 566.
- ¹⁰ E. Campaigne and W. L. Roelfs, J. Org. Chem., 1965, 30, 396.

Cyclisation of the *cis*- and *trans*-acids furnished the *cis*- and *trans*-monoketones (VII) and (X), respectively, and these on further reduction (Wolff-Kishner method and hydrogenolysis were equally effective) gave the corresponding *cis*- and *trans*-hydrocarbons (VIII) and (XI).

Finally, a one step Wolff-Kishner-type reduction of the thermodynamically stable isomer of diketone (III) yielded a hydrocarbon identical in m. p. and vapour phase chromatography, and infrared and n.m.r. spectra, with the *cis*-hydrocarbon (VIII) synthesised as described above.

The n.m.r. spectrum of hydrocarbon (VIII) exhibited a comparatively narrow band in the region between 1.00 and 2.00 p.p.m. as contrasted with a wide envelope of absorption for its isomer (XI). This is a characteristic difference observed for *cis*- and *trans*-decalins.¹¹

More convincing evidence for the hydrocarbons (VIII) and (XI) could be found by investigating the spectral properties of the diketones. In both isomers of the diketone (III) the benzylic type 4a-H, also deshielded by an α -carbonyl group, absorbs at lower field than any other alicyclic proton in the molecule and is easily distinguishable. In diketone (III) before sodium methoxide treatment the 4a-H appears as a doublet centred at δ 3.88 p.p.m. and coupled to 10a-H with J = 10 c./sec. After equilibration the 4a-H is represented by a doublet centred at δ 3.95 p.p.m. and coupled to 10a-H with J = 4.5 c./sec. These two coupling constants for the ring junction hydrogens are consistent with a transand a *cis*-relationship, respectively, thus supporting the cis-B/C fusion for the thermodynamically stable isomer of compound (III).

Similarly, characteristic differences were found in the n.m.r. spectra of the isomers of the 4-monoketone. The *trans*-monoketone (XIV), obtained from *trans*-diketone (III) on hydrogenolysis, exhibited a doublet at δ 3.58 p.p.m. representing the 4a-H coupled to 10a-H with J = 10 c./sec. After treatment with sodium methoxide the *cis*-isomer (XV) was isolated, in which the 4a-H which absorbed at δ 3.70 p.p.m. was coupled to 10a-H with J = 4.5 c./sec.

Assuming that ring B occupies a quasi-chair or even a twist rather than a quasi-boat form, two conformations (XVII) and (XVIII) must be considered for the *cis*fused diketone. Since the *cis*-fused system is relatively flexible, the barrier between the two possible conformers should be low, and both conformers might, therefore, be expected to be present and in rapid equilibrium with each other. Qualitative examination of Dreiding models of each conformation shows that a non-bonded interaction between the 10-H and the 2-H, a known destabilising factor of the *cis- versus trans*-decalin system, is present only in conformation (XVIII), thus indicating a slight preference for (XVII). The choice between these two conformations could be made from n.m.r. data by using the "solvent shift" method. Bhacca and Williams ¹² have reported benzene (solvent) induced chemical shifts in steroidal ketones and acetates and demonstrated the importance of the method



in solving structural and steric problems, mostly in the steroid field.¹³ Similar effects in simpler ketones were recently investigated.¹⁴ It has been concluded that axial protons adjacent to carbonyl are shielded by benzene $[\Delta = \delta(\text{CDCl}_3) - \delta(\text{C}_6\text{H}_6)$ is positive] while the corresponding equatorial protons are either unaffected or deshielded (Δ is negative). These shifts are attributed to the diamagnetic anisotropy of the benzene ring in a solute-solvent collision complex formed by interaction between the π -electrons of the benzene ring and the centre of the partial positive charge of the carbonyl group.¹⁵

Table 1 shows that in the *cis*-diketone the 4a-H experienced a positive shift ($\Delta = +0.27$) in benzene relative to carbon tetrachloride solution, which may be accounted for by its axial character. Thus the solvent shift suggests that *cis*-diketone may exist preferentially in conformation (XVII).

TABLE 1

Solvent shifts $[\Delta = \delta(\text{CCl}_4) - \delta(\text{C}_6\text{H}_6)]$ for bridgehead protons adjacent to carbonyl

Diketone	Proton	$\delta(CCl_4)$	$\delta(C_6H_6)$	$\Delta = \delta(\text{CCl}_4) - \delta(\text{C}_6\text{H}_6)$
cis-	4a-H	(p.p.m.) 3.95	(p.p.m.) 3.68	(p.p.m.) + 0.27
trans	4a-H	3.88	3.43	+0.45

The large solvent shift (+0.45) in the *trans*-diketone (XVI), where the 4a-H occupies *a priori* an axial position, is in full agreement with the above theory.

It was also possible to assign the two CH_3 -signals in the n.m.r. spectra for the respective magnetically non-equivalent methyl groups of the p-xylyl moiety.

The assignments, compiled in Table 2 are based on the following principles: if a C-9 keto-group is present in the molecule, the C-8 CH_3 -group, being in the same plane, lies in the deshielding area of this carbonyl group. Therefore, those CH_3 -signals which appear at lower field in the spectra of the different ketones (VII), (cis- and

J. I. Musher and R. E. Richards, Proc. Chem. Soc., 1958, 230.
 ¹² N. S. Bhacca and D. H. Williams, Tetrahedron Letters, 1964, 3127.

¹³ D. H. Williams and N. S. Bhacca, *Tetrahedron*, 1965, **21**, 1641, 2021.

J. D. Connolly and R. McCrindle, *Chem. and Ind.*, 1965, 379.
 J. V. Hatton and R. E. Richards, *Mol. Phys.*, 1962, 5, 153.

TABLE 3

Effect (Δ_1^* and Δ_2^*) of the carbonyl groups on the CH₃proton resonances in p.p.m.^a

CH _s -group	Octahydrophe	Tetralin	
affected	cis-	trans-	
$5-CH_3$	$(1.1)^{*} = (-0.30)^{*}$	-0.40	<u> </u>
8-CH ₃	Δ_1^{-1} 0.02	0.01	
5-CH ₃	∧ ∗∫ 0·05	0.04	
8-CH ₃	$\frac{2}{2}$ 0.41	0.39	
5-CH3			0.12
8-CH ₃	_	_	0.45
	CH ₃ -group affected 5-CH ₃ 8-CH ₃ 5-CH ₃ 8-CH ₃ 5-CH ₃ 8-CH ₃ 8-CH ₃	$\begin{array}{ccc} {\rm CH}_{{\rm s}}\text{-}{\rm group} & {\rm Octahydrophe} \\ {\rm affected} & {\rm cis-} \\ & {\rm 5-CH}_{{\rm 3}} & {\rm \Delta}_1^{-{\rm s}} \left\{ \begin{array}{c} -0.30 \\ 0.02 \\ 0.02 \\ 0.05 \\ {\rm s-CH}_{{\rm s}} \\ {\rm s-CH}_{{\rm s}} \end{array} \right. \\ & {\rm \Delta}_2^{-{\rm s}} \left\{ \begin{array}{c} 0.00 \\ 0.41 \\ 0.41 \\ 0.41 \\ \end{array} \right. \\ & {\rm s-CH}_{{\rm s}} \end{array} \right. \\ & {\rm s-CH}_{{\rm s}} \end{array}$	$\begin{array}{cccc} {\rm CH}_{3}\text{-}{\rm group} & {\rm Octahydrophenanthrenes} \\ {\rm affected} & {\rm cis-} & {\rm trans-} \\ {\rm 5-CH}_3 & {\rm \Delta_1}^* \left\{ \begin{array}{c} -0.30 & -0.40 \\ 0.02 & 0.01 \\ {\rm 5-CH}_3 & {\rm \Delta_2}^* \left\{ \begin{array}{c} 0.05 & 0.04 \\ 0.41 & 0.39 \\ {\rm 5-CH}_3 & - & - \\ {\rm 8-CH}_3 & - & - \end{array} \right. \end{array} \right.$

 $^{^{\}alpha}$ $\Delta_1{}^*=\delta({\rm CH}_3)$ in the diketones – $\delta({\rm CH}_3)$ in the 9-mono-ketones; $\Delta_2{}^*=\delta({\rm CH}_3)$ in the diketones – $\delta({\rm CH}_3)$ in the 4-monoketones.

Table	4
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Calculated and observed chemical shifts in p.p.m. for the CH₃-protons in the octahydrophenanthrenes

Compound	Resonance	Calculated ^a	Observed
VIII	5-CH,	2.25	$2 \cdot 20$
VIII	8-CH3	$2 \cdot 10$	2.09
XI	5-CH ₃	$2 \cdot 28$	2.22
XI	8-CH ₃	$2 \cdot 11$	2.08

^a The values correspond to the differences: $\delta(CH_s)$ in the 4-monoketones $-\Delta_1^*$, or $\delta(CH_3)$ in the 9-monoketones $-\Delta_2^*$.

monoketone derivative (XX). The single CH3-resonance (2.07 p.p.m.) in the hydrocarbon is replaced by two CH_3 -signals (2.52 and 2.19 p.p.m.) in the ketone. Thus the contribution of the carbonyl group to the CH₃resonances is of a similar order to that of the 9-ketogroup in the octahydrophenanthrene series. (See Table 3.)



EXPERIMENTAL

Ultraviolet spectra were determined on a Perkin-Elmer 137 UV spectrophotometer. N.m.r. spectra were recorded on a Varian A-60 spectrophotometer in carbon tetrachloride solution if not otherwise noted, employing tetramethylsilane as internal reference.

2-(2,5-Xylyl)cyclohexanone (IV).-To 2,5-xylylmagnesium bromide, prepared from 2-bromo-p-xylene (485 g.) and magnesium (63 g.) in dry ether (1200 ml.), 2-chlorocyclohexanone (220 g.) in dry ether (600 ml.) was added at a rate which caused gentle refluxing. The ether was distilled off, replaced by dry benzene (700 ml.), and reflux was continued overnight. The mixture was then decomposed in the cold by adding saturated ammonium chloride solution, followed by a little dilute hydrochloric acid. The organic layer was separated and dried, and the solvent removed. The pure ketone (60 g.) was obtained after vacuum fractionation as a liquid, b. p. 114-118°/0.05 mm. It slowly solidified when kept in the refrigerator, and recrystallised from pentane, m. p. 64-65° (Found: C, 83.3; H, 8.9; O, 8.0. C₁₄H₁₈O requires C, 83.1; H, 9.0; O, 7.9%).

2-(2,5-Xylyl)cyclohexylidenemalononitrile (V).-A mixture of 2-(2,5-xylyl)cyclohexanone (10.0 g.), malononitrile (3.3 g.), ammonium acetate (0.8 g.), acetic acid (2.5 ml.), ¹⁸ K. L. Williamson, L. R. Sloan, Th. Howell, and Th. A. Spencer, *J. Org. Chem.*, 1966, **31**, 436.

trans-III), and (X) must be attributed to the C-8 CH_3 resonance. The chemical shift for this methyl group is practically identical (near 2.50 p.p.m.) both in the diketones (cis- and trans-III) and in the 9-monoketones (VII) and (X). The C-5 CH₃ chemical shifts are, however, markedly different for the same compounds. Since deshielding of this CH3-group, caused by the electronwithdrawing C-9 keto-group, is expected to be about the same in all four ketones, the difference observed in the chemical shift of this CH₃-group in the monoketones, as well as in the diketones, is due totally to the diamagnetic anisotropy of the C-4 carbonyl group in the latter compounds. This effect is evidently a shielding one, and consequently the higher field resonance in the spectra of the monoketones (XIV) and (XV) is assigned to the C-5 CH₃-group.

TABLE 2

Assignments for CH₃ groups

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	C-5 CH ₃	C-8 CH ₃
Compound	(p.p.m.)	(p.p.m.)
<i>cis</i> -(III)	2.00	2.53
trans-(III)	1.92	2.51
(VII)	2.30	2.51
(X)	2.32	2.50
(XV)	1.95	$2 \cdot 12$
(XIV)	1.88	$2 \cdot 12$
(VIII)	$2 \cdot 20$	2.09
(XI)	2.22	2.08

The problem of assigning the chemical shifts of the CH₃-groups in the hydrocarbons (VIII) and (XI) was approached by determining the degree of internal consistency of the additivity effect for the differently located carbonyl groups on the CH₃-resonances of the It has been shown ¹⁶⁻¹⁸ that the p-xylyl moiety. additivity principle is applicable to the angular CH₃group in the steroids and decalins. By using the same principle in our case, the C-5 CH₃-resonance was computed both for cis- and the trans-hydrocarbons (VIII) and (XI) and compared with the observed values. Results are summarised in Table 4. The calculation is exemplified in the *trans* series as follows: The contribution $(\Delta_1^* = -0.40)$ (see Table 3) of the C-4 carbonyl to the C-5 CH₃-resonance, a value necessary for these calculations, may be obtained by subtracting the C-5 CH_3 -shift (2.32 p.p.m.) in the monoketone (X) from the shift (1.92 p.p.m.) of the same CH₃-group in transdiketone (III). Subtraction of this contribution from the C-5 CH₃-shift in monoketone (XIV) [1.88 - (-0.40)]= 2.28] gives the chemical shift expected for the same CH₃-group in *trans*-hydrocarbon (XI). One of the observed values (2.22 p.p.m.) is in good agreement with the calculated one. The degree of consistency in both cis and trans series is sufficiently high to permit assignment for the CH₃-group under discussion.

Supporting evidence was available by comparing the n.m.r. spectra of 5,8-dimethyltetralin (XIX) with the

¹⁶ J. N. Shoolery and M. T. Rogers, J. Amer. Chem. Soc., 1958, 80, 5121.
¹⁷ N. S. Bhacca and D. H. Williams, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day Inc., San Exception Collig. 1964 pp. 144 Francisco, Calif., 1964, p. 14.

and dry benzene (100 ml.) was heated under reflux overnight with stirring, the water produced being removed via an azeotropic collector. The cooled solution was washed with water, followed by dilute sodium carbonate solution until slightly alkaline, dried (Na₂SO₄), and the solvent removed. The brownish gummy residue on trituration with cold methanol gave a yellowish crystalline product (8.0 g.) which could be used without further purification in the following step. Sublimation at 70° (bath)/0.05 mm. followed by crystallisation from hexane gave analytically pure *nitrile*, m. p. 88—90° (Found: C, 80.8; H, 7.5; N, 11.2. C₁₁₇H₁₈N₂ requires C, 81.5; H, 7.25; N, 11.2%).

cis-2-(2,5-Xylyl)cyclohexylacetic Acid (VI).-The unsaturated nitrile (2.5 g.) in methanol (40 ml.) was hydrogenated in the presence of platinum oxide (0.185 g.) at room temperature. Hydrogenation was stopped after consumption of one mole of hydrogen. The catalyst was then filtered off, the solvent evaporated, and the residue heated in a mixture of hydrochloric acid (4 ml.) and glacial acetic acid (8.5 ml.) for 3 days at 100°. After volatile acids had been removed under reduced pressure, ether was added and the solution extracted with N-sodium hydroxide. Acidification of the alkaline layer, re-extraction with ether, followed by evaporation of the dried ether solution gave a crystalline residue (1.35 g.). The analytically pure acid was obtained by sublimation at 90° (bath)/0.05 mm., followed by crystallisation from methylcyclohexane, m. p. 170-172° (Found: C, 78·1; H, 8·9; O, 13·0. C₁₆H₂₂O₂ requires C, 78.0; H, 9.0; O, 13.0%).

2-(2,5-Xylyl)cyclohex-1-enylacetic Acid (XII).—A mixture of the unsaturated dinitrile (V) (0.45 g.), glacial acetic acid (4 ml.), and hydrochloric acid (1 ml.) was heated at 100° for 3 days. The work-up was similar to that described for acid (VI). The oily residue was chromatographed on a column of silica gel (Woelm)–Celite (3:1) (20 g.). Elution with benzene-chloroform (9:1) gave the oily acid, further purified by evaporative distillation at 60° (bath)/0.05 mm.; λ_{max} in MeOH: 240 mµ (ε 2200), 268 mµ (ε 860), 276 mµ (ε 800). The S-benzylthiouronium salt melted at 153—155° (from aqueous ethanol) (Found: C, 69.8; H, 7.2; N, 7.05. C₂₄H₃₀N₂O₂S requires C, 70.2; H, 7.4; N, 6.8%).

cis-1,2,3,4,4a,9,10,10a-Octahydro-5,8-dimethyl-9-oxo-

phenanthrene (VII).—cis-2-(2,5-Xylyl)cyclohexylacetic acid (VI) (1.26 g.) was treated with anhydrous hydrogen fluoride, and after 20 min. air was blown over the mixture to evaporate the hydrogen fluoride. To the residue saturated potassium carbonate solution was added in small portions (carefully) until neutral, and the precipitate was taken up in ether. Evaporation of the solvent gave the monoketone with v_{max} . (in CHCl₃) 1670 cm.⁻¹ (acetophenone-type C:O). It formed a red 2,4-dinitrophenylhydrazone, m. p. 219—221° (from propan-2-ol) (Found: C, 64.6; H, 5.9; O, 15.7; N, 13.7. C₂₂H₂₄N₄O₄ requires C, 64.7; H, 5.9; O, 15.7; N, 13.7%).

cis-1,2,3,4,4a,9,10,10a-Octahydro-5,8-dimethylphenanthrene (VIII).—(a) The crude monoketone (VII) (0.7 g.) was hydrogenated in acetic acid (75 ml.) in the presence of 10% palladised carbon (0.2 g.) at an initial hydrogen pressure of 60 lb./sq. in. After hydrogenation was completed the catalyst and solvent were removed. The crude product was dissolved in hexane and the solution was percolated through neutral alumina (40 g.). The eluate on evaporation gave the solid hydrocarbon (0.4 g.), m. p. 73–75° (from methanol) (Found: C, 89.8; H, 10.2. $C_{16}H_{22}$ requires C, 89.65; H, 10.35%).

(b) Crude diketone (III) was treated with sodium methoxide in methanol and purified by repeated short-path distillation at 120° (bath)/0.08 mm. as described previously.¹ The stable isomer, m. p. 79—80° (1.32 g.), was then reduced by the modified Wolff-Kishner procedure with potassium hydroxide (2.5 g.), 95% hydrazine hydrate (3.7 ml.), and diethylene glycol (31 ml.). After the usual work-up the crude semi-solid (1.25 g.) was chromatographed in hexane on neutral alumina (20 g.). Elution with the same solvent gave white crystals, m. p. 71—72°. Recrystallisation from methanol gave the pure hydrocarbon, identical in m. p., mixed m. p., infrared and n.m.r. spectra, and vapour-phase chromatography (v.p.c.) with the product from procedure (a). trans-1,2,3,4,4a,9,10,10a-Octahydro-5,8-dimethylphen-

anthrene (XI).—trans-1,2,3,4,4a,9,10,10a-Octahydro-5,8-dimethyl-9-oxophenanthrene (X)¹ (1·3 g.) was reduced by the modified Wolff-Kishner procedure with potassium hydroxide (1·6 g.), 95% hydrazine hydrate (2·3 ml.), and diethylene glycol (20 ml.). The oil (1·0 g.) obtained after the usual working up was chromatographed in hexane on neutral alumina (45 g.). Elution with the same solvent gave a milky oil, which after rechromatography solidified (0·7 g.). The pure hydrocarbon melted at 34—35° (Found: C, 89·9; H, 10·3. $C_{16}H_{22}$ requires C, 89·65; H, 10·35%). Mixed m. p. with the *cis*-isomer (m. p. 73—75°) was 26—30°.

Analysis by v.p.c., using a 2 m. $\times \frac{3}{8}$ in. column packed with Silicone Oil QF-1-0065 (10%) on 10—30 mesh Chromosorb P at 180° showed the presence of only one component in the *cis*-isomer. The *trans*-hydrocarbon, on the other hand, was contaminated with about 5% of the *cis*-isomer.

cis- and trans-1,2,3,4,4a,9,10,10a-Octahydro-5,8-dimethyl-4-oxophenanthrenes (XV) and (XIV).-These were prepared in quantities sufficient to record their n.m.r. spectra in the following way. trans-Diketone (III) (0.1 g.) was hydrogenated in acetic acid (50 ml.) in the presence of 10% palladised carbon (0.05 g.) at an initial hydrogen pressure of 60 lb./sq. in. After 12 hr. the catalyst was filtered off and the acid removed under reduced pressure. The oily monoketone (XIV) had ν_{max} (in CHCl₃) 1718 cm.⁻¹ (ali-cyclic C:O). In the n.m.r. spectrum the 4a-H resonance was found at δ 3.88 p.p.m. (doublet, J = 10 c./sec.). The ketone was regenerated from the carbon tetrachloride solution and epimerised in dry methanol (2.0 ml.) with 2N-sodium methoxide in methanol (0.1 ml.) by refluxing for two hr. The usual working up gave the epimeric cis-ketone, $v_{max.}$ (in CHCl₃) 1718 cm.⁻¹ (alicyclic C.O). In the n.m.r. spectrum the 4a-H resonated at 8 3.70 p.p.m. (doublet J = 4.5 c./sec.).

1,2,3,4-Tetrahydro-5,8-dimethylnaphthalene (XIX) and 1,2,3,4-Tetrahydro-5,8-dimethyl-1-oxonaphthalene (XX) were prepared by procedures described in the literature.¹⁹

[6/676 Received, June 1st, 1966]

¹⁹ J. L. Adelfang and N. H. Cromwell, J. Org. Chem., 1961, **26**, 2368; E. de Barry Barnett and F. G. Sanders, J. Chem. Soc., 1933, 434.