

## STEREOCHEMICAL STUDIES. LVIII.\*

SYNTHESIS OF *trans-anti-trans*-PERHYDRO-*as*-INDACENE,  
A SYSTEM CONTAINING  
A "FROZEN" CYCLOHEXANE CHAIR

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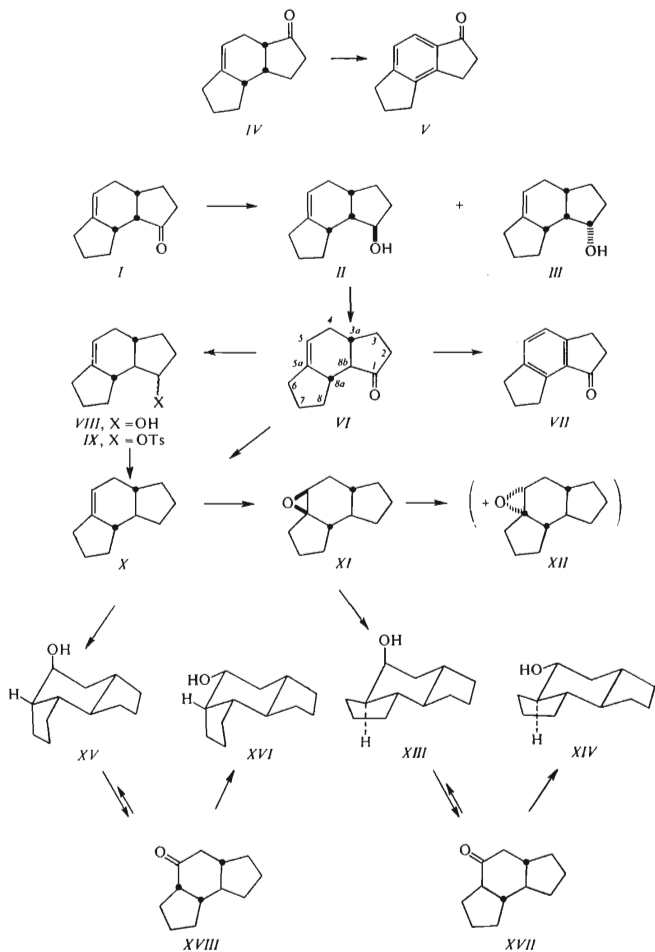
*trans-anti-trans*-Perhydro-*as*-indacene is proposed as a model for studies in which a "frozen" cyclohexane chair (*i.e.* one which can neither flip into the other chair nor into a boat) is required. The synthesis of hydroxy derivatives of this system is reported and evidence establishing their structure is given.

Although cyclohexane is the best understood cyclic system from the conformational point of view, there is some uncertainty regarding the geometry of the cyclohexane ring in the transition state of reactions proceeding on a ring carbon atom. The steric requirements for substitution and elimination reactions are fully met for axial substituents on a cyclohexane chair but not so for equatorial substituents. The possibility has therefore been considered that reactions involving equatorial substituents might proceed by way of a non-chair transition state<sup>1,2</sup> in which the collinearity, or coplanarity, conditions set by the above reaction types could again be met. Thus, non-chair transition states have been postulated for the solvolysis of *trans*-4-*tert*-butylcyclohexyl *p*-bromobenzenesulphonate<sup>3</sup> and cyclohexyl *p*-toluenesulphonate<sup>4</sup>. Boat-like transition states were also suggested for certain bimolecular elimination reactions and reactions with neighbouring group participation involving vicinal diequatorial substituents on related systems<sup>5-7</sup>.

Evidence concerning the course of such processes may be obtained by investigating systems in which the flipping into a boat form is very difficult, or impossible. Attempts in this direction have already been undertaken. Thus, 4,4-dimethylcyclohexyl tosylate has been considered to reproduce rates of a cyclohexane system in which the boat form would be highly strained<sup>8</sup>. However, in view of the known mobility of the cyclohexane boat the arguments are not compelling. It would be better to use a system which would be "frozen" in a single chair conformation.

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SCHEME 1

A careful examination of models shows that such systems are not as frequent as it might be assumed. One such genuine structure is the 2-adamantyl system<sup>9-11</sup> which, while ideal in some respects, has the disadvantage that the secondary carbons are flanked on both sides by tertiary carbons, a feature which makes it impossible to study reactions involving a neighbouring atom.

In a search for a model which would allow studies of "two center reactions", we found the cyclohexane ring in *trans-anti-trans*-perhydro-*as*-indacene system to fulfil these requirements. Although the *trans*-annellation to the two five-membered rings may induce some puckering in the cyclohexane, models suggest that this cannot be very serious. We therefore set out to synthesise some derivatives of this system.

The carbon skeleton of decahydro-*as*-indacene was constructed in one step employing the Diels-Alder condensation of 1-vinylcyclopentene with cyclopentenone, by analogy with earlier syntheses by Nazarov and coworkers<sup>12,13</sup> (Scheme 1). The reaction affords a mixture from which the unsaturated ketone *I* is readily isolated by chromatography on silica gel.

The ketone *I* on treatment with methanolic sodium methoxide gave the epimeric ketone *VI*. The structure of the two isomeric ketones was established as follows. Dehydrogenation of *VI* using sulphur gave the known ketone *VII*, whose structure was confirmed by an independent synthesis<sup>14</sup>. The configuration of the centers 3a, 8a and 8b in *I* was shown to be *cis*(3a,8b)-*syn*(8b,8a) by reducing *I* and examination the infrared spectra in the OH region of the resulting alcohols *II* and *III*. As may be seen on models, of all the possible configurational isomers only the *cis-syn* isomer *III* can exhibit an intramolecular hydrogen bond (cf. Fig. 1). With the configuration of *I* being established, the configuration of *VI* must be as shown in the formula. The overall yield of *VI* from the cyclopentenone (without isolating intermediates) is 48%.\* Reduction of *VI* to *X* was effected by two methods: by Wolf-Kishner reduction, and by hydride reduction of the ketone *VI*, followed by tosylation and hydride reduction.

Two alternative routes were employed for completing the synthesis of the desired *trans-anti-trans* system. In the first we examined the hydroboration of *X*. This

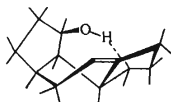


FIG. 1

Intramolecular Hydrogen Bond in the *cis-syn*-isomer *III*

\* In addition to the 1-oxo-decahydro-*as*-indacene system, the Diels-Alder product contained the position isomeric system *IV*, as revealed by the presence of the 3-oxo-1,2,3,6,7,8-hexahydro-*as*-indacene (*V*) (ref.<sup>15</sup>), in the dehydrogenation product of the crude reaction mixture.

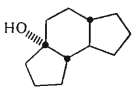
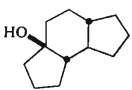
reaction could have led either to the desired *trans-anti-trans* alcohol *XIV* (OH equatorial) or to the *cis-anti-trans* compound *XV* (OH axial). Unfortunately, the hydroboration gave in stereospecific reaction an alcohol, melting at 83.5–84°C, which was shown to possess the *cis-anti-trans* configuration *XV* (*vide infra*). The epimeric alcohol *XVI* was obtained by the usual oxidation–reduction sequence. This approach having failed we converted the key olefin *X* to the epoxide *XI*; this was obtained together with about 10% of the epimeric epoxide *XII* by direct epoxidation. Reduction of the epoxide using diborane in tetrahydrofuran<sup>16</sup> gave the alcohol *XIII*, whereas reductions using lithium aluminium hydride or  $\text{LiAlH}_4 : \text{AlCl}_3$  gave only minor amounts of the required alcohol, the main product being tertiary alcohols (Table I). The other alcohol *XIV* was again obtained by oxidation followed by reduction.

It remained to determine the configuration on the centres  $\text{C}_{(3a)}$  and  $\text{C}_{(4)}$  in the alcohols *XIII* and *XV*. This assignment will also establish the configuration of the other two alcohols, *XIV* and *XVI*. This was done by comparison of the NMR spectra of the alcohols, making use of different chemical shifts and band widths of equatorial and axial tertiary protons under the OH group<sup>17,18</sup>. Thus, the spectrum of the alcohol *XIII* from reduction of the epoxide exhibited  $\delta = 4.13$  p.p.m. (multiplet,  $\Sigma J = 7$  c.p.s.) whereas the epimeric compound *XIV* had  $\delta = 3.47$  p.p.m. (multiplet,  $\Sigma J = 25$  c.p.s.). (Table II). This clearly shows that in the alcohol which arises from the epoxide the hydroxyl is axial and hence belongs to the *trans-anti-trans* series. On the other hand,

TABLE I

Comparison of the Reduction Products of the Epoxide *XI* (Containing 12% of the Epimeric Epoxide *XII*) with Various Reagents (in %)

Configurations can be assigned to the two tertiary alcohols on the basis of the known configuration and relative amounts of the epoxides *XI* and *XII*. The alcohols were detected only as peaks in vapour phase chromatograms and were not isolated in a pure state.

Reagent			<i>XIII</i>	<i>XVI</i>
$\text{LiAlH}_4$	13	84	3	0
$\text{AlH}_3$	12	50	38	0
$\text{B}_2\text{H}_6$ ( $\text{LiBH}_4$ )	8	8	81	3

the alcohol formed by hydroboration had  $\delta = 3.99$  p.p.m. (multiplet,  $\Sigma J = 7$ ) and its epimer *XVI* has  $\delta = 3.98$  p.p.m. (multiplet,  $\Sigma J = 25$ ), which suggests that the hydroboration product has an axial hydroxyl and therefore has the structure *XV*. Replacement of the hydrogen in the 3a position with deuterium<sup>19</sup> in compounds *XIII* and *XIV* resulted in  $\delta = 4.05$  (multiplet,  $\Sigma J = 7$ ) and  $\delta = 4.04$  (multiplet,  $\Sigma J = 7$ ), respectively. These data closely parallel those found for the analogous 4-tert-butyl-2-methylcyclohexanols<sup>18,20</sup> ( $\text{CH}_3^e\text{OH}^e$ :  $\delta = 3.05$  p.p.m.,  $\Sigma J = 25$ ;  $\text{CH}_3^e\text{OH}^e$ :  $\delta = 3.74$  p.p.m.,  $\Sigma J = 9$ ;  $\text{CH}_3^e\text{OH}^e$ :  $\delta = 3.66$  p.p.m.,  $\Sigma J = 10$ ;  $\text{CH}_3^a\text{OH}^e$ :  $\delta = 3.67$  p.p.m.,  $\Sigma J = 20$ ).

TABLE II

Chemical Shifts and Band Widths for the Carbinol Hydrogens in the Alcohols *XIII*–*XVI*

Measured on a Varian HA-100 spectrometer in deuteriochloroform with tetramethylsilane as standard.

Compound	$\delta$ p.p.m.	$\Sigma J$ c.p.s. (multiplet)
<i>XIII</i>	4.13	7
<i>XIV</i>	3.47	25
<i>XV</i>	3.99	7
<i>XVI</i>	3.98	25
<i>XIII</i> , 3a- $d_1$	4.05	7
<i>XIV</i> , 3a- $d_1$	4.04	7

TABLE III

Percentages of the Alcohols *XIII*–*XVI* Present at Equilibrium Aluminium 2-propoxide in 2-propanol at 160°C.

Starting alcohol	<i>XIII</i>	<i>XIV</i>	<i>XV</i>	<i>XVI</i>
<i>XIII</i>	12.9	46.3	22.8	18.0
<i>XIV</i>	13.9	45.8	22.6	17.7
<i>XV</i>	12.6	44.7	22.8	19.9
<i>XVI</i>	12.7	44.8	23.4	19.1
Mean	13.0	45.4	22.9	18.7

It was of interest to determine the relative stability of the *trans-anti-trans* and the *cis-anti-trans* systems. Alkali-catalysed equilibration at 64°C revealed a preference of the *cis-anti-trans* ketone XVIII over the epimeric ketone XVII, corresponding to an energy difference  $\Delta G$  of about 1.5 kcal/mol. On the other hand, "complete" equilibration of the alcohols XIII—XVI showed the *trans-anti-trans* system (alcohols XIII and XIV) to be more stable, corresponding to  $\Delta G \sim 0.3$  kcal/mol. This suggests that the main strain in the *trans-anti-trans* ketone is due to the angle strain introduced by the  $sp^2$ -hybridised carbon. The ratio at equilibrium of the equatorial to the axial alcohol in the *trans-anti-trans* series (*i.e.* XIV to XIII) is 3.5 (Table III); this corresponds almost exactly to the OH-equatorial to OH-axial ratio found by us previously in the 3-methyl-*trans*-2-decalols and the 2-methyl-4-*tert*-butylcyclohexanols<sup>21</sup>. This close correspondence represents valuable support for our view that the chair form of the cyclohexane moiety in the *trans-anti-trans*-perhydro-*as*-indacene system is not seriously deformed and its use as a cyclohexane model therefore is justified.

Studies on reactions of the alcohols XIII and XIV and their derivatives will be reported in a subsequent paper.

## EXPERIMENTAL

### 1-Oxo-*trans*(3a,8b)-*anti*(8a,8b)-1,2,3,3a,4,6,7,8,8a,8b-decahydro-*as*-indacene (VI)

A mixture of 3-cyclopentenone<sup>22</sup> (370 g, 4.5 mol), 1-vinylcyclopentene<sup>23,24</sup> (450 g, 4.78 mol) and hydroquinone (0.5 g) was heated in an autoclave at 150°C for 8 hours. Fractional distillation of the reaction mixture afforded non-reacted cyclopentenone (135 g) boiling at 64–65°C/35 Torr and 516 g of the adduct, b.p. 90–92°C/0.5 Torr. The distilled adduct (516 g) was boiled with methanolic sodium methoxide (made by dissolving 25 g of sodium in 3 l of methanol) for 5 hours under nitrogen. The cold solution was poured into ice-cold water (8 l), extracted four times with light petroleum, the organic layer washed with water and taken to dryness. The crystalline residue, after one recrystallisation from pentane (–50°C) and two from ligroin, melted at 72–73°C and weighed 243 g (48.2%). IR spectrum (tetrachloromethane):  $\nu(\text{CO})$  1741  $\text{cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$  1668  $\text{cm}^{-1}$ , 3015  $\text{cm}^{-1}$ . For  $\text{C}_{12}\text{H}_{16}\text{O}$  (160.3) calculated: 81.77% C, 9.15% H; found: 81.68% C, 9.01% H.

### 1-Oxo-*cis*(3a,8b)-*syn*(8b,8a)-1,2,3a,4,6,7,8,8a,8b-decahydro-*as*-indacene (I)

The distilled product from the Diels-Alder reaction (3.9 g) was chromatographed on silica gel (800 g). Elution with benzene afforded as the first ketonic fraction 1.9 g of an oil, boiling at 95°C/0.5 Torr which sets to a crystalline mass upon cooling and melts at 0–2°C. IR spectrum (tetrachloromethane):  $\nu(\text{CO})$  1740  $\text{cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$  1665, 3040  $\text{cm}^{-1}$ . For  $\text{C}_{12}\text{H}_{16}\text{O}$  (176.3) calculated: 81.77% C, 9.15% H; found: 81.84% C, 9.10% H. When refluxed with 0.5M methanolic sodium methoxide (5 ml) for 5 hours the ketone I (0.4 g) is converted in 75% yield into the ketone VI, m.p. 72–73°C.

### 1-Oxo-1,2,3,6,7,8-hexahydro-*as*-indacene (VII)

A) A mixture of the ketone VI, m.p. 72–73°C (1.2 g) and flowers of sulphur (0.45 g) was heated at 190–200°C for 45 minutes. The reaction mixture was extracted with ether, the extract taken

to dryness and the residue chromatographed on silica gel (50 g). The elution with pentane-ether (4 : 1) gave 0.4 g of a compound which after two crystallisations from ligroin melted at 88–88.5°C, undepressed on admixture with an authentic sample of *VII* prepared according to the literature<sup>14</sup>. UV-spectrum: (ethanol) 214 nm (17.800), 251 nm (12.300), 310 nm (2.800). For  $C_{12}H_{12}O$  (172.2) calculated: 83.69% C, 7.02% H; found: 83.66% C, 7.08% H.

*Tosylhydrazone*, m.p. 170–172°C (dec.; ethanol), on admixture with the tosylhydrazone of 3-oxo-1,2,3,6,7,8-hexahydro-*as*-indacene it melts at 157–168°C (dec.)

*B*) The distilled reaction mixture after the Diels-Alder condensation (0.5 g) was dehydrogenated with sulphur (0.2 g) at 190–200°C. Chromatographic separation on silica gel (50 g) afforded two principal fractions: the compound *VII*, m.p. 88–89°C (ligroin); and a compound, m.p. 107–108°C (ligroin), UV-spectrum (ethanol): 212 nm (17.000), 220 nm (20.000), 262 nm (12.900), essentially in accord with the spectrum published by Rapoport<sup>15</sup> for the 3-oxo-1,2,3,6,7,8-hexahydro-*as*-indacene (*V*). Its tosylhydrazone melted at 223–224°C (dec.) (inserted into Kofler block at 180°C) either alone or admixed with an authentic sample of *V*.

*cis*- and *trans*-1-Hydroxy-*cis*(3a,8b)-*syn*(8b,8a)-1,2,3,3a,4,6,7,8,8a,8b-decahydro-*as*-indacene (*II* and *III*)

The *cis-syn* ketone *I* (1.0 g) was reduced with lithium aluminium hydride (0.3 g) in ether (30 ml). The usual work-up procedure gave 1.0 g of a semicrystalline mass which, according to vapour phase chromatography and thin layer chromatography, consisted of two compounds which could be separated by chromatography on silica gel (70 g) using pentane-ether (4 : 1) as eluent. The first was an oil (0.3 g), b.p. 78°C/0.5 Torr, IR spectrum ( $5 \cdot 10^{-3}M$ , tetrachloromethane):  $\nu(OH)$  3622i (free OH), 3567s (bonded OH) and is hence assigned structure *III*. For  $C_{12}H_{18}O$  (178.3) calculated: 80.85% C, 10.18% H; found: 80.18% C, 10.06% H. The second, the crystalline alcohol *II*, (0.6 g), had m.p. 68–69°C (light petroleum), IR spectrum ( $5 \cdot 10^{-3}M$ , tetrachloromethane):  $\nu(OH)$  3628s, 3612i (free OH). For  $C_{12}H_{18}O$  (178.3) calculated: 80.85% C, 10.18% H; found: 81.02% C, 10.24% H.

*trans-anti*-1,2,3,3a,4,6,7,8,8a,8b-Decahydro-*as*-indacene (*X*)

*A*) By *Wolf-Kishner reaction*: The ketone *VI* (125 g) and 80% hydrazine hydrate (70 ml) in methanol (300 ml) were refluxed for 1.5 hour. The usual work-up procedure gave 120 g (89%) of the hydrazone, m.p. 87–89°C (cyclohexane). For  $C_{12}H_{18}N_2$  (190.3) calculated: 75.74% C, 9.53% H, 14.72% N; found: 75.54% C, 9.68% H, 14.91% N.

A mixture of the hydrazone (120 g), potassium hydroxide (100 g) and diethylene glycol (500 ml) was heated at 200°C and 100 Torr, the product being continuously distilled off. The distillate was shaken between pentane and water, the organic layer passed through an aluminium oxide column (grade II) and the product after evaporation of the solvent distilled, b.p. 100–101°C/10 Torr, m.p. 9–10°C,  $n_D^{20}$  1.5060, yield 85.1 g (83%). IR spectrum: 831, 1671, 3020  $cm^{-1}$  (trisubstituted double bond). For  $C_{12}H_{18}$  (162.3) calculated: 88.82% C, 11.18% H; found: 88.58% C, 11.16% H.

*B*) via *Tosylate*: The ketone *VI* (21.5 g) was reduced with lithium aluminium hydride (4.0 g) in ether (150 ml). After decomposition with water and 15% sodium hydroxide, the hydroxides were filtered off and digested four times with boiling ether. A sample of the reduction product was sublimed *in vacuo*, giving a solid, m.p. 104–119°C. Vapour phase chromatography of this sample shows two nearly coalescent peaks. IR spectrum ( $5 \cdot 10^{-3}M$ , tetrachloromethane):  $\nu(OH)$

3629s, 3614i (free OH). For  $C_{12}H_{18}O$  (162.3) calculated: 80.85% C, 10.18% H; found: 81.09% C, 10.19% H. After evaporation of the solvent, the residue (21.5 g) was dissolved in pyridine (70 ml), treated with *p*-toluenesulphonyl chloride (30.0 g) under cooling, and allowed to stand overnight. The usual isolation procedure afforded 38.5 g (96%) of the tosylate.

The crude tosylate was dissolved in ether (120 ml) and the solution added to a stirred suspension of lithium aluminium hydride (7.0 g) in ether (200 ml) at such a rate as to keep the solution boiling gently. After the addition, the stirred mixture was boiled for 3 hours. The reaction mixture was worked up as usual, the crude product passed through a silica gel column (activated, 40 g) and distilled, b.p. 106–107°C/9 Torr, m.p. 8–9°C (in bulk). Yield 17.3 g (92%). According to vapour phase chromatography, the olefin contains about 2% of an impurity of longer retention time, presumably a diene.

*cis*-3a,4-Epoxy-*anti*(8a,8b)-*trans*(8a,5a)-perhydro-*as*-indacene (XI)

The usual perphthalic acid (13.5 g) epoxidation of the olefin *X* (10.0 g) in ether (120 ml) yielded the epoxide XI, b.p. 82°C/0.3 Torr (9.8 g, 89%), which contained, according to vapour phase chromatography, about 12% of the epimeric epoxide XII. For  $C_{12}H_{18}O$  (178.3) calculated: 80.85% C, 10.18% H; found: 81.09% C, 10.21% H.

*cis*-4-Hydroxy-*cis*(3a,8b)-*anti*(8a,8b)-*trans*(5a,8a)-perhydro-*as*-indacene (XV)

The olefin *X* (6.5 g) in diglyme (50 ml) was subjected to the usual hydroboration procedure, using sodium borohydride (0.8 g) and boron trifluoride etherate (4.0 g). Aqueous 8% sodium hydroxide (5 ml) was added, followed by 30% hydrogen peroxide (6.0 ml), and the mixture was stirred for 1 hour. The reaction was worked up in the usual way, the product which was shown by vapour phase chromatography to contain one principal component, was crystallised twice from pentane, thus yielding the alcohol XV, m.p. 83.5–84°C, yield 4.5 g (69%). For  $C_{12}H_{20}O$  (180.3) calculated: 79.94% C, 11.18% H; found: 79.84% C, 11.31% H.

4-Oxo-*cis*(3a,8b)-*anti*(8a,8b)-*trans*(5a,8a)-perhydro-*as*-indacene (XVIII)

The alcohol from the above preparation (1.0 g) was oxidised in acetone (10 ml) by adding the Jones' reagent at 0°C till the consumption of chromium trioxide ceased. The usual isolation and distillation at 72–73°C/0.3 Torr gave 0.9 g (90%) of the oily ketone XVIII. For  $C_{12}H_{18}O$  (178.3) calculated: 80.85% C, 10.18% H; found: 80.70% C, 10.24% H.

*trans*-4-Hydroxy-*cis*(3a,8b)-*anti*(8a,8b)-*trans*(5a,8a)-perhydro-*as*-indacene (XVI)

Lithium aluminium hydride reduction of the ketone XVIII gave, in a 8:92 ratio, a mixture of the alcohols XV and XVI from which the latter, m.p. 87.5–88°C, was obtained pure by crystallisation from ligroin. For  $C_{12}H_{20}O$  (180.3) calculated: 79.94% C, 11.18% H; found: 80.05% C, 11.15% H.

4-Oxo-*trans*(3a,8b)-*anti*(8a,8b)-*trans*(5a,8a)-perhydro-*as*-indacene (XVII)

To a stirred solution of lithium borohydride (6.0 g) in tetrahydrofuran (200 ml) was added boron trifluoride etherate (7.5 g) in tetrahydrofuran (50 ml) under nitrogen. After 30 minutes, a solution of the epoxide XI (25.0 g) in tetrahydrofuran (50 ml) was added slowly and the mixture was



stirred for 3 hours at room temperature. The mixture was decomposed with 1M-H<sub>2</sub>SO<sub>4</sub> (75 ml) under cooling, treated with anhydrous potassium carbonate and decanted from the solid which was triturated with ether. After distilling off the solvent *in vacuo*, the residue was dissolved in light petroleum, washed with water, dried and taken down *in vacuo*. The composition of the product mixture is given in Table I. From this mixture it was possible either to obtain the alcohol *XIII* by chromatography on silica gel or — by direct oxidation with Jones' reagent — to prepare the ketone *XVII* which was further purified by chromatography (using 1 kg silica gel for 25 g of the mixture; eluent ether-pentane 1 : 6). In this manner, 25 g of the epoxide afforded 18.1 g (72% overall yield) of the ketone *XVII*, m.p. 41.5–42.5°C (pentane, –50°C). For C<sub>12</sub>H<sub>18</sub>O (178.3) calculated: 80.85% C, 10.18% H; found: 80.79% C, 9.93% H.

#### Equilibration of the Ketones *XVII* and *XVIII*

Each of the ketones (0.1 g) was refluxed with methanolic sodium methoxide (from 0.1 g Na in 5 ml methanol) for 2 hours, the mixture decomposed with ice-cold water, extracted with pentane, and the extract after drying taken down at 0°C *in vacuo*. As the ketones did not separate on vapour phase chromatography, they were reduced with lithium aluminium hydride to the alcohols which were then analysed. The analysis gives the same ratio, *i.e.* (*XIII* + *XIV*) : (*XV* + *XVI*) = = *XVII* : *XVIII* = 10 : 90, starting from either side.

#### *cis*-4-Hydroxy-*trans*(3a,8b)-*anti*(8a,8b)-*trans*(5a,8a)-perhydro-*as*-indacene (*XIV*)

The reduction of the ketone *XVII* (1.0 g) with lithium aluminium hydride (0.25 g) afforded a mixture of the alcohols *XIII* and *XIV* in a 26 : 74 ratio, from which the alcohol *XIV*, m.p. 122–122.5°C (0.60 g) was isolated by two crystallisations from ligroin. A further amount (0.10 g) was obtained by chromatography of the mother liquor (*vide infra*). IR spectrum (5.10<sup>-3</sup>M, tetrachloromethane):  $\nu(\text{OH})$  3625 cm<sup>-1</sup>. For C<sub>12</sub>H<sub>20</sub>O (180.3) calculated: 79.94% C, 11.18% H; found: 80.00% C, 11.19% H.

#### *trans*-4-Hydroxy-*trans*(3a,8b)-*anti*(8a,8b)-*trans*(5a,8a)-perhydro-*as*-indacene (*XIII*)

A) The compound *XIII* (0.10 g) was obtained as the first fraction in the chromatography of the mother liquors from the above crystallisation: it melts at 59–60°C. IR spectrum (5.10<sup>-3</sup>M, tetrachloromethane):  $\nu(\text{OH})$  3632 cm<sup>-1</sup>. For C<sub>12</sub>H<sub>20</sub>O (180.3) calculated: 79.94% C, 11.18% H; found: 80.14% C, 11.22% H.

B) The tosylate of the alcohol *XIV* (1.7 g) was heated in dry molten tetrabutylammonium acetate (7.0 g) at 120°C for 5 hours, the cold reaction mixture was taken up in water, extracted with ether, the organic layer washed with dilute hydrochloric acid and water. After drying and evaporation of the solvent, the crude crystalline acetate (m.p. 66–68°C) was reduced with lithium aluminium hydride (0.3 g) in ether (10 ml), affording after the usual work-up procedure isomerically completely pure *XIII*, m.p. 59–60°C, in 87% yield.

#### The Equilibration of the Alcohols *XIII*–*XVI*

The equilibration<sup>21</sup> was performed at 160°C. The amount of the equilibrated alcohol is 0.06 mmol instead of 0.6 mmol. The analyses were carried out at 140°C on a 3.4 m column, packed with a 1 : 1 mixture of 1,2,3,4-tetrakis-(2-cyanoethoxy)butane and poly(butylene glycol adipate) on Chromosorb. The results are summarised in Table III.

We are greatly indebted to Professor H. Rapoport, University of California, Berkeley, for a gift of the tosylhydrazone of oxo-as-hydrindacene and to Dr M. Masojdková for measuring the NMR spectra.

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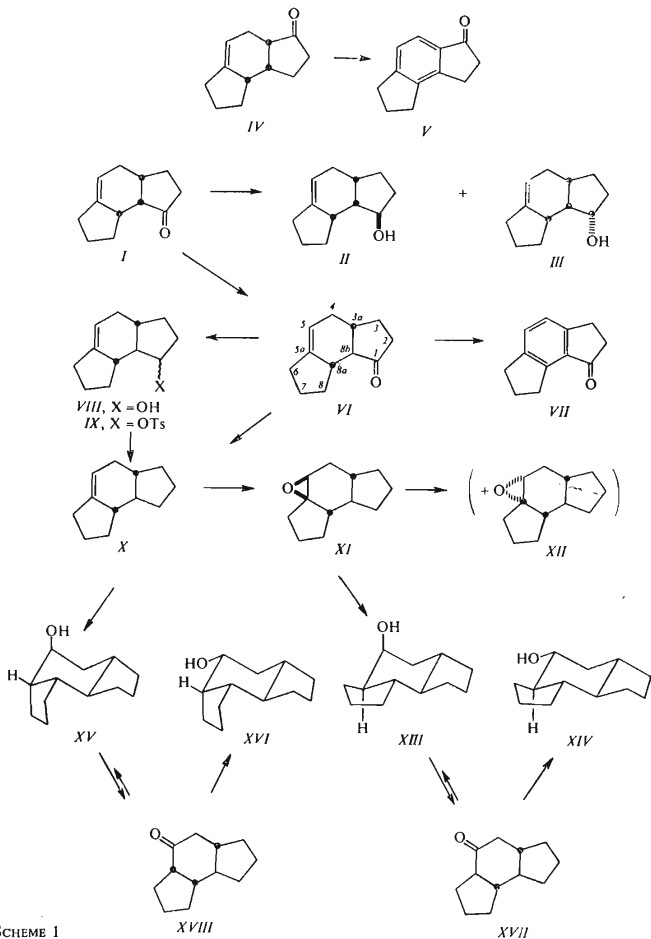
Translated by the author (M. T.).

## STEREOCHEMICAL STUDIES. LVIII.

SYNTHESIS OF *trans-anti-trans*-PERHYDRO-*as*-INDACENE,  
A SYSTEM CONTAINING "FROZEN" CYCLOHEXANE CHAIR

M.TICHÝ and J.SICHER

This Journal 36 (1971), p. 1427, Scheme 1 is to be replaced by the following scheme:



SCHEME 1