Tricyclic [10]annulenes. Part 3.[1] Reactions of 7b-Methyl-7b*H*-cyclopent[*cd*]indene

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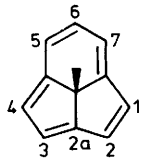
The chemical reactions of the tricyclic [10]annulene (1) are described. The annulene is rapidly hydrogenated to give the fully saturated hydrocarbon (2). It undergoes a substitution reaction with electrophiles and has been nitrated, acetylated, formylated, and sulphonated. The preferential sites of attack of electrophiles are C-5 and C-1. Although the annulene (1) does not undergo cycloaddition reactions with tetracyanoethylene, dimethyl acetylenedicarboxylate, or benzyne, it does react with 4-phenyl-1,2,4-triazole-3,5-dione in refluxing 1,2-dimethoxyethane to give the 2:1 adduct (17) and with chlorosulphonyl isocyanate to give the ring-expanded indenoazepine (19). Hydrolysis of (19) gives the amide (20), which shows some antiaromatic character.

The synthesis of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) is reported in the preceding paper.[1] The physical properties of (1) support its formulation as a 10π-aromatic system. We now report in detail the chemical reactions of the [10]annulene (1), with particular regard to its electrophilic substitution reactions.[2]



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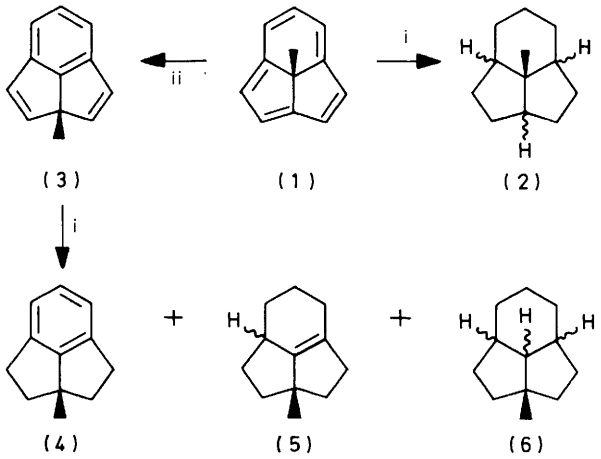
Hydrogenation.—The annulene (1) is readily hydrogenated over 5% palladium-on-carbon catalyst at atmospheric pressure. Five equivalents of hydrogen were rapidly taken up to give the fully saturated hydrocarbon(s) (2) as a colourless oil (Scheme 1). The ^{1}H n.m.r. spectrum supported the structure (2), and mass spectrometry confirmed the uptake of five equivalents of hydrogen. This facile reduction of an aromatic system under mild conditions is probably a result of the ring strain present in (1). This effect of strain is also seen in the catalytic hydrogenation of the related 2a*H*-isomer (3), formed by thermal rearrangement of (1).[1] An initial rapid uptake of hydrogen was followed by a slow uptake. The mass spectrum showed that the product was a mixture of compounds arising from the uptake of 2, 4, and 5 equivalents of hydrogen, and the product structures are tentatively assigned as (4), (5), and (6). Thus the effect of strain in compound (3) is to make the normally resistant benzene ring susceptible to facile hydrogenation. That such tri-substituted benzenes are indeed strained has been clearly demonstrated by an *X*-ray study of the related hydrocarbon, fluoradene, which showed that the benzene ring deviates considerably from planarity.[3]

Electrophilic Substitution.—One of the most characteristic chemical properties associated with aromaticity, as exemplified by the archetypal aromatic compound benzene, is the tendency to undergo substitution rather than addition reactions with electrophiles. In keeping with its aromatic character, the tricyclic [10]annulene (1) also undergoes electrophilic substitution reactions.

Nitration. Reaction of (1) with copper(II) nitrate in acetic anhydride[4] at 0 °C gave a mixture of all four possible mononitrated products (41% total). These could not be completely separated, but careful column chromatography gave two fractions which could be analysed by n.m.r. spectroscopy. The first (orange) fraction was a mixture of the 1- and 2-nitroannulenes, and the second (yellow) fraction was a mixture of the 5- and 6-nitro derivatives. The ratio of products (Table 1) indicates a distinct preference for 1- and 5-substitution. No dinitrated products were observed, and lowering the reaction temperature did not alter the product composition significantly.



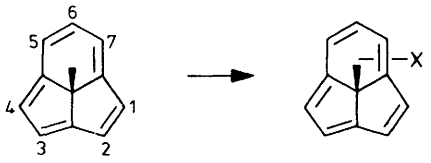
Scheme 1. *Reagents:* i, H_2, 5% Pd–C, EtOH; ii, flash vacuum pyrolysis at 400 °C/0.3 mmHg

It is reported that for mononitration of azulene, tetranitromethane in pyridine is the preferred reagent.[5] However, using this reagent, the annulene (1) was slowly consumed to give dark base-line material. A trace of a mixture of mononitro compounds could be detected by t.l.c. Use of dimethyl sulphoxide as solvent gave similar results.

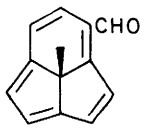
In contrast, reaction of the annulene (1) with the nitronium trifluoromethanesulphonate–collidine complex[6] gave an unexpected result. A mixture of mononitrated annulenes was slowly formed in poor yield. Analysis of the mixture by n.m.r. spectroscopy showed it to be a 2:1 mixture of the 6-isomer and the 2-isomer. These are the two isomers which are normally formed to the least extent, and this unusual selectivity may be the result of steric control by the hindered reagent, or a completely different mechanism may be operating.

Reduction of the mixture of the nitroannulenes formed in the copper(II) nitrate reaction with zinc in acetic anhydride gave a corresponding mixture of acetamidoannulenes (54%)

Table. Product composition in electrophilic substitution reactions of annulene (1)



X	Reagent	Percentage distribution 1-	2-	5-	6-	Yield (%)
NO_2	$Cu(NO_3)_2$·Ac_2O	40	5	40	15	41
NO_2	$NO_2CF_3SO_3$·collidine	0	33	0	66	5
$COCH_3$	Ac_2O·BF_3	20	0	75	5	55
CHO	Cl_2CHOBu^n·$SnCl_4$	4	0	93	3	28
SO_3Na	SO_3			>95		70



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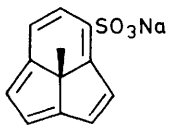

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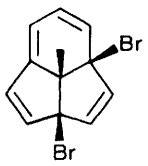

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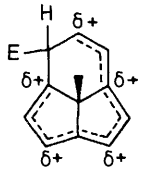

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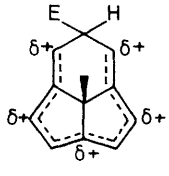

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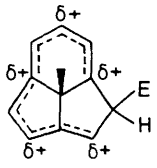

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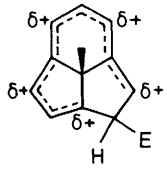

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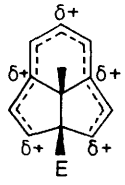


(14)

as an unstable semisolid. Reduction with zinc in acetic acid gave a complex mixture.

Acetylation. The annulene (1) was acetylated by treatment with acetic anhydride in dichloromethane catalysed by boron trifluoride–ether.[4] The reaction, which was completed in 3 h at room temperature, was more selective than nitration and gave a higher yield of monoacetylated products (Table 1).

Formylation. Formylation of the annulene (1) with dichloromethyl n-butyl ether and tin(IV) chloride in dichloromethane [4] at −78 °C was more selective still, and gave the 5-carbaldehyde (7) almost exclusively. The mauve 2,4-dinitrophenylhydrazone of (7) was isolated pure. However, despite the selectivity, the low overall yield (28%) of the formylation precluded the use of (7) as a precursor to other 5-substituted annulenes.

Attempts to benzoylate the annulene (1) with benzoyl chloride and aluminium chloride [4] were not successful.

Sulphonation. Sulphonation of (1) was also very selective. The annulene was consumed immediately when added to a solution of sulphur trioxide in dioxane [7] at 12 °C. The product was isolated as its sodium salt, a yellow hygroscopic solid, the n.m.r. spectrum of which showed that it was almost pure 5-monosulphonate (8). The product was characterised as its *S*-benzylthiouronium salt.

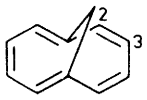
Bromination. Reaction of the annulene (1) with *N*-bromosuccinimide in dimethylformamide gave poor recovery of material and no recognisable products. In contrast, treatment with pyridinium bromide perbromide in benzene, a reagent used successfully for the bromination of [18]annulene,[8] gave a clean reaction. However, no substitution products were isolated and the crystalline dibromide (9) was the major (78%) product. This product is probably formed by initial electrophilic attack at C-2a. The resulting carbocation is then intercepted at another bridgehead position by the excess of bromide ion present. The dibromide (9) can be converted back into the [10]annulene (1) by treatment with activated zinc in ether.

The annulene (1) also reacted with bromine in carbon tetrachloride, but a mixture of products was formed, none of which was identified.

The preference for 5- and 1-substitution can be rationalised in terms of the carbocation intermediates involved (10)—(14). The intermediate cation (10) formed by attack of the electrophile, E^+, at the 5-position should be more stable than the cation (11) formed by attack at the 6-position since the positive charge can be delocalised onto two tertiary positions in (10) but onto only one in (11). Similarly 1-substitution (12) should be favoured over 2-substitution (13). That substitution occurs to a greater extent at the 6- than the 2-position is possibly due to the enhanced symmetry of intermediate (11).

The intermediate (14), formed by attack at the 2a-position, is stabilised by two tertiary centres and is symmetrical. More importantly, attack at the 2a-position relieves the strain associated with this sp^2 centre. It is therefore to be expected that attack by electrophiles at the 2a-position should be favoured, and it is likely that reasonable yields of substitution products only result when this initial addition is reversible, as for example with sulphonation where reversibility is well known. Therefore it is concluded the reactivity of the positions in the annulene (1) towards electrophiles follows the order: 2a > 5 > 1 > 6 > 2. This is in accord with calculations which predict that the likely site of protonation is C-2a.[9]

The selectivity of the related system, 1,6-methano[10]-annulene (15), towards electrophiles has been measured by detritiation and desilylation. Those studies conclude that the 2-position is much more reactive than the 3-position as a consequence of the significant transannular homoaromatic interaction in (15).[10] Thus, although nitration of (15) with copper(II) nitrate gives a mixture of 2- and 3-substituted products, selective 2-nitration can be achieved using the



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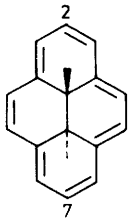


(16)

nitronium trifluoromethanesulphonate-collidine complex.[6] The sulphonation and bromination of (15) also contrast with those of (1). Whereas sulphonation of (1) gives >95% 5-substitution, under the same conditions (15) gives disubstituted products.[7] Bromination of (15) does give a substitution product, although the mechanism involves addition of bromine followed by elimination of hydrogen bromide.[11]

In contrast, nitration of the tetracyclic [14]annulene (16) gave the symmetrical 2-nitro derivative as the only product.[4]

Thermal Rearrangement of 5-Substituted Annulenes.—When heated in solution the annulene (1) and its 2-monosubstituted derivatives rearrange by a [1,5]sigmatropic shift of the central methyl to the corresponding 2a-methyl isomers.[1] The 5-substituted annulenes (7) and (8) rearrange similarly when heated, although measurement of the rates of methyl migration, by the u.v. method described previously,[1] gave unexpected results. The aldehyde (7) rearranges in decalin at the same rate as the parent annulene (1) ($t_{\frac{1}{2}}$ 12 h at 138 °C). This is in contrast to the 2-carbaldehyde which rearranged much faster under the same conditions ($t_{\frac{1}{2}}$ 1.1 h at 138 °C).[1] One possible explanation is that the rate is increased relative to the unsubstituted annulene when partial carbocation character can be induced or stabilised at the terminus of migration (C-2a). When the formyl group is in the 5-position it is not conjugated with C-2a and is too far away to have a significant inductive effect.

The rearrangement of the sulphonate (8) could not be followed in non-polar solvents owing to its insolubility. In diethylene glycol, the sulphonate rearranged surprisingly fast ($t_{\frac{1}{2}}$ 7 h at 138 °C). However, it was then found that the parent annulene (1) rearranged just as fast in this solvent, again demonstrating the negligible effect of a 5-substituent on the rate of rearrangement. The rate of migration does show a slight solvent effect in that it is accelerated by a protic solvent. These results perhaps suggest that there is some charge separation in the transition state, and the reaction is accelerated when this can be stabilised by a suitable solvent. However, use of a dipolar aprotic solvent (dimethyl sulphoxide) caused no increase in rate.[1]

Cycloaddition Reactions.—In so far as the annulene (1) formally contains a cyclopentadiene unit, it could undergo cycloaddition reactions. Indeed the related 1,5-methano[10]-annulene does give [2 + 2]-cycloadducts with tetracyanoethylene (TCNE),[12] dimethyl acetylenedicarboxylate (DMAD) [12] and benzyne.[13] The DMAD and benzyne adducts then underwent ring expansion to give 12π-systems.[12,13] However, the annulene (1), in keeping with its delocalised character, did not give adducts with DMAD, maleic anhydride, or with benzyne (generated by thermolysis of benzenediazonium-2-carboxylate). With TCNE the annulene (1) gave reversible formation of a green charge-transfer complex. There was no adduct formation and the annulene was recovered unchanged after being heated with a large excess of TCNE in 1,2-dimethoxyethane (DME).

Although the annulene (1) did not react with the powerful dienophile, 4-phenyl-1,2,4-triazole-3,5-dione (PTAD), at room temperature, in refluxing DME the crystalline 2 : 1 adduct (17) was formed in 75% yield. No 1 : 1 adduct was detected even when a deficiency of PTAD was used, indicating that the initial olefinic 1 : 1 adduct must, not surprisingly, be more reactive towards PTAD than the annulene. The structure of the adduct (17) was deduced from nuclear Overhauser effect (n.O.e.) measurements in the ^{1}H n.m.r. spectrum (see Figure). Irradiation of the central methyl group caused a strong enhancement of all the protons originating from the periphery of the annulene, proving that the methyl group is still in the central position and that both PTAD groups are on the opposite face of the molecule to the methyl. A molecular model shows that the PTAD units lie in nearly parallel planes, and it is likely that the direction of approach of the second PTAD molecule is controlled by secondary orbital interactions between the incoming dienophile and the PTAD unit in the 1 : 1 adduct. Similar interactions are reported in the addition of PTAD to propellanes,[14] and to 1,6-methano[10]annulene (15).[15] In the latter case, cycloaddition occurs at room temperature to give a mixture of 1 : 1 and 2 : 1 adducts. The greater facility of addition of PTAD to (15) than to (1) is further evidence for the significant transannular interaction in (15); such an interaction plays little or no role in the chemistry of (1).

Reaction of the annulene (1) with chlorosulphonyl isocyanate (CSI) in dichloromethane at 0 °C gave a single product, a deep red solid. By analogy with the reaction of CSI with annulene (15) in which the CSI acts as an electrophile to give the corresponding 2-substituted annulene,[6] reaction with (1) was expected to give the corresponding 5-substituted annulene. However, the red product showed a methyl resonance at δ 1.94 in the n.m.r. spectrum which rules out an annulene structure. On the basis of this relatively lowfield signal for methyl on sp^3 carbon, the product was assigned the ring-expanded structure (19). The formation of (19) is explained by formal [2 + 2] cycloaddition of CSI to the annulene to give (18) followed by a ten-electron ring opening as shown in Scheme 2. Although the initial addition is a formal [2 + 2] addition it is likely that it proceeds by attack of the electrophilic CSI at C-2a followed by collapse of the dipolar species to give (18).

The adduct (19) was somewhat resistant to hydrolysis, although the amide (20) was formed by hydrolysis with aqueous sodium sulphite and sodium hydroxide. The amide (20) is an unstable green solid which gives mauve solutions, and in its n.m.r. spectrum the methyl group resonates at δ 3.06, and the olefinic protons are shifted to higher field relative to (19). The n.m.r. data is consistent with the presence of some paramagnetic ring current due to the 12π-electron periphery of (20). The adduct (19) shows less paratropic effect since electron withdrawal by the chlorosulphonyl group causes the nitrogen lone pair to be less available for contribution to the ring system. It should be emphasised that the amide (20) only shows a very small degree of 12π-character. In general, the chemical shift of groups experiencing a ring current in the n.m.r. spectrum is much more sensitive to the downfield shift caused by paramagnetic effects than the upfield shift caused by diamagnetic effects. In fully antiaromatic systems very large downfield shifts are observed. For example in the 16π-dianion derived from the [14]annulene (16), the central methyl groups resonate at δ 21.0.[16]

The amide (20) rearranges by a [1,5] sigmatropic shift of the methyl group with a half-life of less than 10 s in refluxing xylene, just over 1 min in refluxing toluene, and 17 min in refluxing benzene. It is not surprising that the rearrangement is so fast since a benzenoid product (21) is being formed from

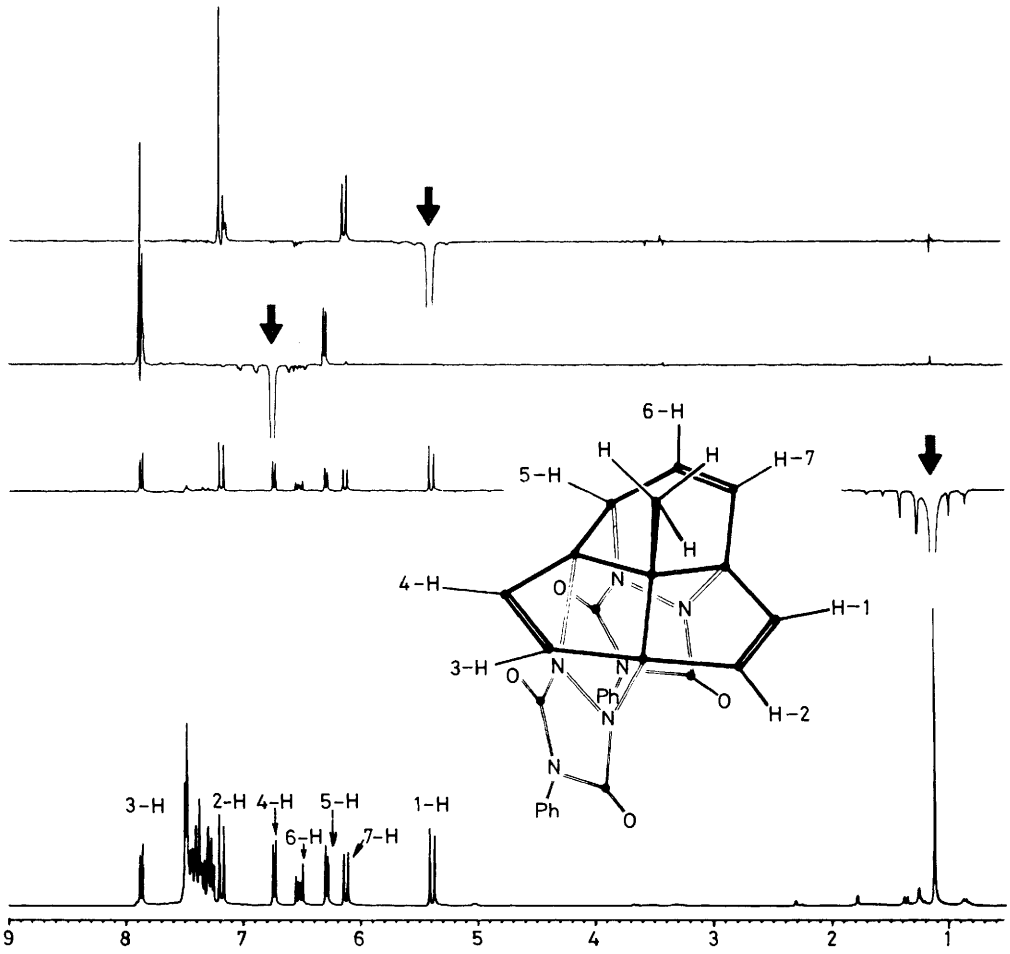


Figure. 250 MHz ^{1}H N.m.r. spectrum of the adduct (17) and n.O.e. results (position of pre-irradiation indicated by arrow)

an antiaromatic starting material. The product of the rearrangement (21) is a stable colourless crystalline solid.

The chlorosulphonyl compound (19) also rearranges when heated (half-life 8.3 min) in refluxing toluene. However, when this rearrangement was followed by u.v. spectroscopy in the usual way [1] a small peak at 450 nm appeared. This absorption results from the formation of the annulene (1) and suggests that the addition and ring-opening process shown in Scheme 2 are reversible. When cyclohexene was added to intercept the liberated CSI, the isolated yield of (1) was 42% (Scheme 3). In the absence of cyclohexene the major product was the expected rearranged adduct (22), together with traces of annuleneamides. These annuleneamides are presumably formed by addition of the liberated CSI to (1) at a non-bridgehead position.

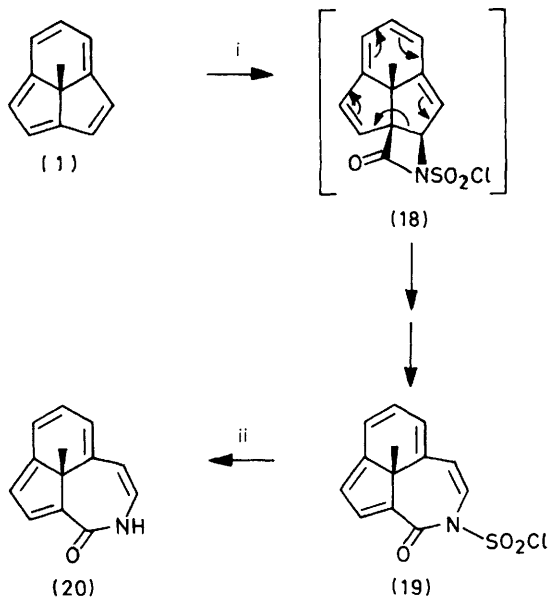
The indenoazepines (19) and (20) are the first examples of a tricyclic [5-6-7] system with a conjugated 12π-periphery. The parent hydrocarbon (23) would obviously be of interest and, in principle, could be prepared by [2 + 2] addition of a suitable two-carbon unit to the annulene (1). Unfortunately (1) did not react with dichloroketene. The failure of (1) to react with TCNE, DMAD, and benzyne has already been described.

Other Reactions.—Electron transfer. The annulene (1) did not form a picrate. When concentrated solutions of (1) and picric acid in ethanol were mixed, the resulting solution was orange suggesting the formation of a change-transfer complex, both components being yellow. However, no solid complex could be isolated even on concentrating the solution. The non-formation of a solid picrate is not too surprising since the angular methyl group would be expected to prevent the stacking of layers in the crystal. The tetracyclic [14]annulene (16) does not form a picrate either.[4]

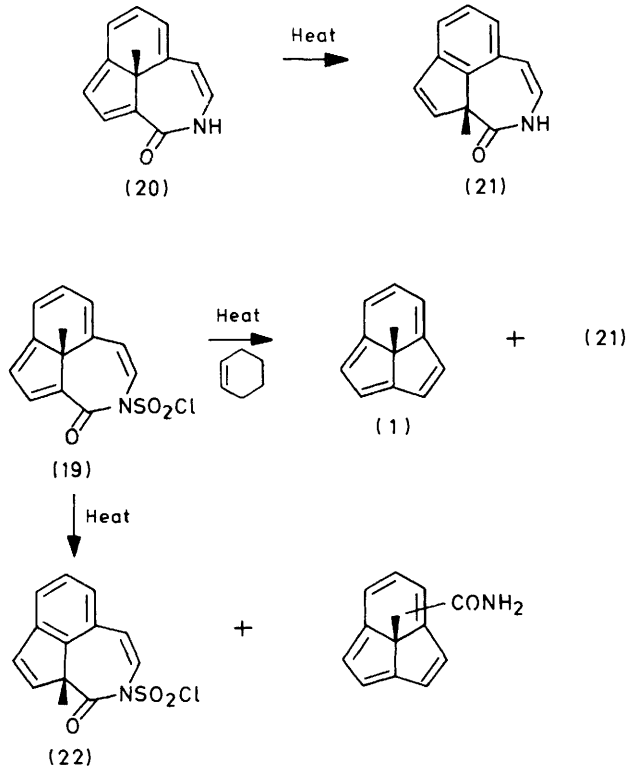
Potassium metal dissolved in a solution of the annulene (1) in tetrahydrofuran to give a deep red solution. This solution was unstable and turned brown with time. When a solution of the annulene was added to a solution of sodium in liquid ammonia, and the resulting orange mixture quenched with ammonium chloride, a mixture of olefinic hydrocarbons was formed. No individual products could be identified. In contrast, the [14]annulene (16) cleanly gave the symmetrical 2,7-dihydro derivative on Birch reduction.[4]

Lithiation. Attempts to lithiate the annulene (1) were unsuccessful. There was no reaction with n-butyl-lithium in petroleum, but when tetramethylethylenediamine was added, the annulene was consumed to give a deep red solution. However, after quenching with carbon dioxide and subsequent acidification, no annulenecarboxylic acids could be detected. A yellow olefinic product was formed, and its n.m.r. spectrum showed that a butyl group had been incorporated. No structure could be assigned to this product and it was probably a mixture. The annulene (1) reacted only slowly with t-butyl-lithium and, after carbonation, again no products could be identified.

Metal complexes. Preliminary results suggest that the annulene (1) does not form π-complexes with metals which accept 4 or 6 electrons. Apart from decomposition of the

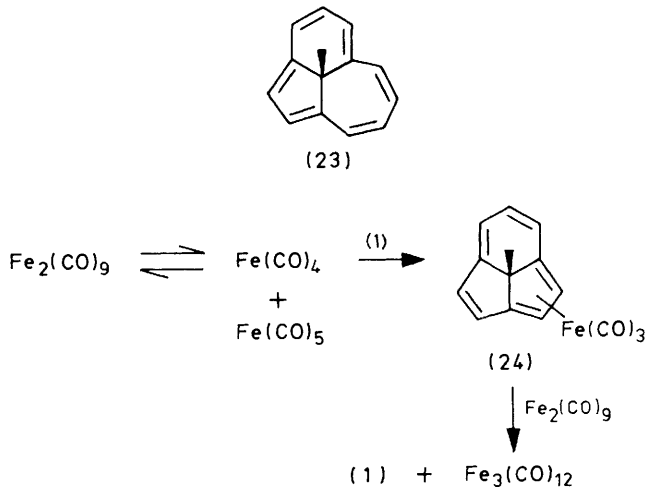


Scheme 2. *Reagents:* i, CSI, CH_2Cl_2, 0 °C; ii, Na_2SO_3, NaOH, H_2O, room temp.



Scheme 3.

reagent, there was no reaction with hexacarbonylchromium in a refluxing mixture of di-n-butyl ether and tetrahydrofuran (3 : 1). With nonacarbonyldi-iron in benzene at 50 °C, the reaction mixture became dark green, and dodecacarbonyltri-iron could be isolated. Although no annulene was consumed, the dodecacarbonyltri-iron was not formed in the absence of the annulene. Hence, the annulene seems to catalyse the transformation of nonacarbonyldi-iron, and this possibly involves an unstable tricarbonyliron complex (24).



Experimental

For general points see ref. 1.

Hydrogenation of 7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1).—The annulene (1) (22.9 mg, 0.15 mmol) was introduced to a shaken suspension of 5% palladium-on-charcoal (55 mg) in ethanol (12 ml) under an atmosphere of hydrogen at 750 mmHg and 16.1 °C. Hydrogenation was complete in 0.5 h when 16.72 ml (0.75 mmol, 5.0 equiv.) of hydrogen had been taken up. The reaction mixture was filtered through Celite and the filtrate poured into water (100 ml) and extracted with petroleum (3 × 50 ml). The combined extracts were washed with water (50 ml), dried ($MgSO_4$), and evaporated to give *decahydro*-7b-*methyl*-1H-*cyclopent*[cd]*indene* (2) (14.1 mg, 58%) as a colourless oil (Found: *m/z* 164.1562. $C_{12}H_{20}$ requires *m/z* 164.1565); δ_H (250 MHz, $CDCl_3$) 1.13 (3 H, s, 7b-Me) and 1.0—1.7 (17 H, m); *m/z* 164 (M^+), 149, 136, 135, and 121.

Hydrogenation of 2a-*Methyl*-2aH-*cyclopent*[cd]*indene* (3).—A solution of (3) (*ca.* 8 mg) in ethanol (12 ml) was hydrogenated over 5% palladium-on-charcoal (11 mg) at 751 mmHg and 16.5 °C. Accurate readings for the quantity of hydrogen taken up were not obtained but it was apparent that there was a fairly rapid uptake (*ca.* 0.5 h), followed by a much slower uptake. After 24 h, the mixture was filtered through Celite, and the solvent evaporated to give an oil. Mass spectrometry showed ions at *m/z* 158, 162, and 164 with corresponding $M^+ - 15$ ions at *m/z* 143, 147, and 149.

Nitration of the Annulene (1) *with Copper*(II) *Nitrate.*—A solution of the annulene (1) (29.9 mg, 0.194 mmol) in acetic anhydride (2 ml) was treated with powdered copper(II) nitrate trihydrate (47 mg, 0.194 mmol), and the mixture stirred at 0 °C. After 40 min, the mixture was poured into ice–water (10 ml) and extracted with ether (3 × 5 ml). The combined ether layers were washed with saturated aqueous sodium hydrogencarbonate (20 ml), dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave (i) a 10 : 1 mixture of 7b-*methyl*-1-*nitro*-7bH-*cyclopent*[cd]*indene* and 7b-*methyl*-2-*nitro*-7bH-*cyclopent*[cd]-*indene* (6.7 mg, 17%) as an orange-red oil, $\nu_{max.}$ (CCl_4) 1 378, 1 338, and 1 304 cm^{-1}; $\lambda_{max.}$ (EtOH) 246 (log ε 4.18), 307 (4.11), 332sh (3.88), 402 (3.75), and 485 nm (3.19); δ_H (250 MHz, $CDCl_3$) for the 1-nitro isomer: −1.27 (3 H, s, 7b-Me), 7.72 (1 H, d, *J* 7.3 Hz, 5-H), 7.89 (1 H, t, *J* 7 Hz, 6-H), 8.08 (1 H, d, *J* 3.5 Hz, 4-H), 8.23 (1 H, d, *J* 7.5 Hz, 7-H), 8.29 (1 H, d, *J* 3.5 Hz, 3-H), and 8.33 (1 H, s, 2-H). The signals for the

2-nitro isomer are obscured by those of the 1-isomer except for 7.69 (1 H, t, *J* 7 Hz, 6-H), 7.81 (1 H, d, *J* 7.3 Hz, 5-H), and 8.01 (1 H, d, *J* 7.6 Hz, 7-H). The mixture gives *m/z* 199 (M^+), 182, 169, 153, and 152 (base). (ii) A 2 : 1 mixture of 7b-*methyl*-5-*nitro*-7bH-*cyclopent*[cd]*indene* and 7b-*methyl*-6-*nitro*-7bH-*cyclopent*[cd]*indene* (9.1 mg, 24%) as a yellow-orange oil, $\nu_{max.}$ (CCl_4) 1 320 cm^{-1}; $\lambda_{max.}$ (EtOH) 248sh (log ε 3.95), 275 (4.15), 315 (4.22), 376 (3.82), 444sh (3.19), and 482 nm (3.07); δ_H (250 MHz, $CDCl_3$) for the 5-nitro isomer: −1.32 (3 H, s, 7b-Me), 7.71 (1 H, d, *J* 8.2 Hz, 7-H), 7.99 (1 H, d, *J* 3 Hz, 1-H), 8.14 (1 H, d, *J* 3.3 Hz, 2-H), 8.20 (1 H, d, *J* 3.3 Hz, 3-H), 8.48 (1 H, d, *J* 8.2 Hz, 6-H), and 8.50 (1 H, d, *J* 3.3 Hz, 4-H); for the 6-nitro isomer: −1.35 (3 H, s, 7b-Me), 8.00 (2 H, d, *J* 3 Hz, 2-H and 3-H), 8.29 (2 H, d, *J* 3.5 Hz, 1-H and 4-H), and 8.62 (2 H, s, 5-H and 7-H).

Nitration of the Annulene (1) *with Nitronium Trifluoromethanesulphonate.*—A stirred suspension of nitronium trifluoromethanesulphonate [17] (36 mg, 0.18 mmol) in dichloromethane (2 ml) was treated with collidine (23 mg, 0.19 mmol) at 0 °C under nitrogen. After 0.5 h at room temperature, a solution of the annulene (1) (28 mg, 0.18 mmol) in dichloromethane (2 ml) was added, and the mixture refluxed for 4 h. The mixture was cooled, evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave the starting annulene (1) (15 mg, 42% recovery). Elution with petroleum–ether (19 : 1) gave a 2 : 1 mixture of 7b-methyl-6-nitro-7b*H*-cyclopent[*cd*]indene and 7b-methyl-2-nitro-7b*H*-cyclopent[*cd*]indene.

Reduction of the Nitroannulenes.—A solution of the mixed nitroannulenes (22.6 mg) in acetic anhydride (2 ml) was treated with sodium acetate (100 mg) and zinc dust (200 mg) at room temperature. The mixture was stirred for 10 min, poured into water (30 ml), and extracted with ether (3 × 15 ml). The combined ether extracts were washed with saturated aqueous sodium hydrogencarbonate (20 ml), dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (7 : 3) gave a mixture of *acetamidoannulenes* (13.0 mg, 54%), as an unstable yellow semisolid, δ_H (90 MHz, $CDCl_3$) −1.45 (3 H, s, 7b-Me) and 7.4—8.0 (6 H, m); *m/z* 211 (M^+), 169 (base), and 168.

Acetylation of the Annulene (1).—A solution of the annulene (1) (10.1 mg) in dichloromethane (3 ml) was treated with acetic anhydride (0.25 ml) and boron trifluoride–ether (2 drops). The mixture was stirred at room temperature for 3.5 h, and then poured into water (10 ml). The aqueous layer was separated and extracted with dichloromethane (10 ml). The combined organic layers were dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (17 : 3) gave 15 : 5 : 1 mixture of 5-, 1-, and 6-acetyl-7b-methyl-7b*H*-cyclopent[*cd*]indenes (6.9 mg, 54%) as an orange oil, $\nu_{max.}$ (CCl_4) 1 672 cm^{-1}; $\lambda_{max.}$ (EtOH) 305, 347, 450sh, and 477 nm; δ_H (250 MHz, $CDCl_3$) for the 5-acetyl isomer: −1.47 (3 H, s, 7b-Me), 2.87 (3 H, s, Ac), 7.69 (1 H, d, *J* 7.5 Hz, 7-H), 7.93 (1 H, d, *J* 3.3 Hz, 1-H), 8.05 (1 H, d, *J*, 3.3 Hz, 2-H or 3-H), 8.08 (1 H, d, *J* 3.3 Hz, 3-H or 2-H), 8.22 (1 H, d, *J* 7.4 Hz, 6-H), and 8.38 (1 H, d, *J* 3.3 Hz, 4-H); for the 1-acetyl isomer: −1.42 (3 H, s, 7b-Me), 2.82 (3 H, s, Ac), 7.67 (1 H, d, *J* 6.8 Hz, 5-H), 7.75 (1 H, t, *J* 7 Hz, 6-H), 7.97 (1 H, d, *J* 3.3 Hz, 4-H), 8.06 (1 H, d, 7-H), 8.12 (1 H, d, *J* 3.3 Hz, 3-H), and 8.27 (1 H, s, 2-H); for the 6-acetyl isomer: −1.44 (3 H, s, 7b-Me), 2.81 (3 H, s, Ac), 7.90 (2 H, d, *J* 3.3 Hz, 2-H and 3-H), 8.14 (2 H, d, *J* 3.3 Hz, 1-H and 4-H), and 8.31 (2 H, s, 5-H and 7-H); *m/z* 196 (M^+, base), 181, and 153.

Formylation of the Annulene (1).—A stirred solution of the annulene (1) (52 mg, 0.33 mmol) in dichloromethane (3 ml) containing dichloromethyl n-butyl ether [18] (100 mg, 0.64 mmol) was cooled to −78 °C under nitrogen, and treated with tin(IV) chloride (0.05 ml). The mixture immediately became dark blue. After 10 min, the mixture was poured into water (50 ml), and the mixture shaken until the blue colour was discharged. The products were extracted with ether (3 × 20 ml). The combined extracts were washed with water (20 ml), dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave the starting annulene (1) (3 mg, 4% recovery). Elution with petroleum–ether (4 : 1) gave 7b-*methyl*-7bH-*cyclopent*[cd]*indene*-5-*carbaldehyde* (7) (*ca.* 93% pure, contains 4% of the 1-carbaldehyde and 3% of the 6-isomer); δ_H (250 MHz, $CDCl_3$) −1.42 (3 H, s, 7b-Me), 7.74 (1 H, d, *J* 7.6 Hz, 7-H), 7.96 (1 H, d, *J* 3.4 Hz, 1-H), 8.07 (1 H, d, *J* 7.6 Hz, 6-H), 8.08 (1 H, d, *J* 3.4 Hz, 2-H), 8.11 (1 H, d, *J* 3.4 Hz, 3-H), 8.40 (1 H, d, *J* 3.4 Hz, 4-H), and 10.43 (1 H, s, C*H*O).

Treatment of this mixture of aldehydes with 2,4-dinitrophenylhydrazine in ethanol acidified with concentrated sulphuric acid gave an immediate precipitate of hydrazones (81%). Repeated recrystallisation gave the 2,4-*dinitrophenylhydrazone of aldehyde* (7) as mauve needles, m.p. 201.5—203.5 °C (from acetonitrile–dimethylformamide, 1 : 1) (Found: C, 62.9; H, 3.9; N, 15.4. $C_{19}H_{14}N_4O_4$ requires C, 63.0; H, 3.9; N, 15.45%).

Sulphonation of the Annulene (1).—A solution of the annulene (1) (74 mg, 0.48 mmol) in dry dioxane was added to a stirred solution of freshly generated sulphur trioxide (200 mg, 2.5 mmol) in dry dioxane (5 ml) at 12 °C under nitrogen. After 20 min, the mixture was poured into aqueous sodium carbonate (5% w/v; 40 ml), and washed with dichloromethane (30 ml). The aqueous layer was evaporated to dryness and the residue was extracted exhaustively with hot ethanol. Evaporation of the ethanol gave *sodium* 7b-*methyl*-7bH-*cyclopent*-[cd]*indene*-5-*sulphonate* (8) (86 mg, 70%) as a hygroscopic yellow solid, δ_H [(250 MHz, $(CD_3)_2SO$)] −1.69 (3 H, s, 7b-Me), 7.66 (1 H, d, *J* 7.6 Hz, 7-H), 7.83 (1 H, d, *J* 7.6 Hz, 6-H), 7.94 (1 H, d, *J* 3.4 Hz, 1-H or 2-H), 7.99 (1 H, d, *J* 3.4 Hz, 2-H or 1-H), 8.01 (1 H, d, *J* 3.4 Hz, 3-H), and 8.23 (1 H, d, *J* 3.4 Hz, 4-H).

Treatment of this salt with a solution of *S*-benzylthiouronium chloride in water acidified with dilute hydrochloric acid (0.1M; 1 drop) at room temperature gave an immediate precipitate of the S-*benzylthiouronium salt* as yellow needles, m.p. 195—197 °C (from water) (Found: C, 60.1; H, 5.05; N, 7.0; S, 16.2. $C_{20}H_{20}N_2S_2O_3$ requires C, 60.0; H, 5.05; N, 7.0; S, 16.0%).

Bromination of the Annulene (1).—A solution of the annulene (1) (38 mg, 0.25 mmol) in benzene (10 ml) was treated with pyridinium bromide perbromide (79 mg, 0.25 mmol). The mixture was stirred at room temperature until the colour of the reagent was discharged (1 h). The mixture was washed with dilute sulphuric acid (1M; 10 ml) and water (10 ml), dried (Na_2SO_4), and evaporated to give 2a,4a-*dibromo*-4a,7b-*dihydro*-7b-*methyl*-2aH-*cyclopent*[cd]*indene* (9) (60 mg, 78%) as pale yellow crystals, m.p. 123—124.5 °C (from cold petroleum) (Found: C, 46.0; H, 3.15. $C_{12}H_{10}Br_2$ requires C, 45.9; H, 3.2%); $\nu_{max.}$ (CCl_4) 3 060, 1 450, 1 372, 1 142, 918, 862, and 654 cm^{-1}; $\lambda_{max.}$ (EtOH) 326 nm (log ε 3.46); δ_H (250 MHz, $CDCl_3$) 1.43 (3 H, s, 7b-Me), 5.80 (1 H, br d, *J* 5 Hz, 7-H), 5.83 (1 H, dd, *J* 5.1 Hz, 8.6 Hz, 6-H), 5.97 (1 H, dd, *J* 1.2 Hz, 8.6 Hz, 5-H), 6.03 (1 H, d, *J* 5.6 Hz), 6.17 (1 H, d, *J* 5.8 Hz), 6.19 (1 H, d, *J* 5.6 Hz), and 6.39 (1 H, d, *J* 5.8 Hz);

m/z 316—314—312 (1 : 2 : 1, M^+), 235—233 (1 : 1, M^+ − Br), 154 (base), 153, and 149.

Reaction of the Annulene (1) *with* 4-*Phenyl*-1,2,4-*triazole*-3,5-*dione* (*PTAD*).—A solution of the annulene (1) (34 mg, 0.22 mmol) and PTAD [19] (78 mg, 0.44 mmol) in freshly distilled 1,2-dimethoxyethane (10 ml) was refluxed under nitrogen for 1 h. Evaporation of the solvent, and chromatography of the residue on silica gel gave the *adduct* (17) (85 mg, 75%) as fine needles which decompose at 150 °C without melting (from 1 : 1 : 1 ethyl acetate–ether–petroleum) (Found: C, 66.6; H, 4.0; N, 16.6. $C_{28}H_{20}N_6O_4$ requires C, 66.65; H, 4.0; N, 16.65%); $\nu_{max.}$ (CCl_4) 1 794, 1 776, 1 724, and 1 408 cm^{-1}; $\lambda_{max.}$ (EtOH) 242sh (log ε 3.96) and 290sh nm (3.49); δ_H (250 MHz, $CDCl_3$) 1.13 (3 H, s), 5.40 (1 H, d, *J* 10.0 Hz, 1-H), 6.13 (1 H, d, *J* 9.0 Hz, becomes a singlet on decoupling at 6.53, 7-H), 6.30 (1 H, d, *J* 5.5 Hz, 5-H), 6.53 (1 H, dd, *J* 5.5 Hz, 9.0 Hz, 6-H), 6.75 (1 H, d, *J* 6.0 Hz, becomes a singlet on decoupling at 7.80, 4-H), 7.20 (1 H, d, *J* 10.0 Hz, becomes a singlet on decoupling at 5.40, 2-H), 7.23—7.53 (10 H, m, 2 × Ph), and 7.89 (1 H, d, *J* 6.0 Hz, 3-H).

Reaction of the Annulene (1) *with Chlorosulphonyl Isocyanate* (*CSI*).—A stirred solution of the annulene (1) (243 mg, 1.57 mmol) in dichloromethane (20 ml) was treated with CSI (0.15 ml, 240 mg, 1.7 mmol) at 0 °C. After 25 min at 0 °C, the dark-red mixture was poured into ice–water (100 ml). The aqueous layer was extracted with dichloromethane (30 ml), and the combined organic layers were dried (Na_2SO_4), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave the starting annulene (1) (62 mg, 25% recovery). Elution with petroleum–ether (1 : 1) gave N-*chlorosulphonyl*-2,9b-*dihydro*-9b-*methyl*-1H-*indeno*[1,7-cd]-*azepin*-1-*one* (19) (219 mg, 47%; 63% based on consumed starting material) as red flakes, m.p. 160—162 °C (from petroleum–dichloromethane) (Found: *m/z* 295.0075. $C_{13}H_{10}{}^{35}ClNO_3$ requires *m/z* 295.0070); $\nu_{max.}$ (CCl_4) 1 712, 1 690, 1 490, 1 410, 1 188, 1 134, 1 100, 1 030, 1 010, 852, 678, 632, and 614 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 232 (log ε 4.05), 299 (4.42), and 484 nm (3.02); δ_H (250 MHz, $CDCl_3$) 1.93 (3 H, s, 9b-Me), 5.79 (1 H, d, *J* 5.8 Hz, 5-H), 5.82 (1 H, d, *J* 9.5 Hz, 4-H), 6.03 (1 H, d, *J* 9.5 Hz, 3-H), 6.20 (1 H, dd, *J* 5.8 Hz, 9.4 Hz, 6-H), 6.37 (1 H, d, *J* 2.9 Hz, 8-H), 6.50 (1 H, d, *J* 9.4 Hz, 7-H), and 7.89 (1 H, d, *J* 2.9 Hz, 9-H); *m/z* 297—295 (1 : 3, M^+), 282—280 (1 : 3, $M^+ - CH_3$), 254—252 (1 : 3, $M^+ - CH_3 - CO$), 231, 197, 196, 162, and 154 (base).

Hydrolysis of the Chlorosulphonamide (19).—A solution of the chlorosulphonamide (19) (101 mg) in dichloromethane (10 ml) was stirred with a mixture of aqueous sodium sulphite (5% w/v; 5 ml) and aqueous sodium hydroxide (5% w/v; 3 ml). After 5 h at room temperature, the aqueous layer was discarded, and the organic layer was washed with water (10 ml), dried (Na_2SO_4), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (1 : 1) gave starting material (6 mg, 6% recovery). Elution with petroleum–ether (1 : 4) gave 2,9b-*dihydro*-9b-*methyl*-1H-*indeno*[1,7-cd]*azepin*-1-*one* (20) (53 mg, 79%) as a dark brown-green solid (Found: *m/z* 197.0840. $C_{13}H_{11}NO$ requires *m/z* 197.0841); $\nu_{max.}$ (CCl_4) 3 420, 3 225, 3 090, 2 980, 1 669, 1 628, 1 344, and 912 cm^{-1}; $\lambda_{max.}$ (EtOH) 229 (log ε 3.72), 275 (4.11), 343 (3.41), and 550br nm (2.16); δ_H (250 MHz, $CDCl_3$) 3.06 (3 H, s, 9b-Me), 4.53 (1 H, d, *J* 10.2 Hz, 4-H), 4.84 (1 H, d, *J* 6.0 Hz, 5-H), 5.02 (1 H, dd, *J* 7.0 Hz, 10.2 Hz, 3-H), 5.48 (1 H, dd, *J* 6.0 Hz, 9.7 Hz, 6-H), 5.68 (1 H, d, *J* 2.5 Hz, 8-H), 5.74 (1 H, d, *J* 9.7 Hz, 7-H), 6.3 (1 H, br, NH), and 6.91 (1 H, d, *J* 2.5 Hz, 9-H); *m/z* 197 (M^+, base), 196, 182, and 154.

Thermal Rearrangement of the Amide (20).—A solution of the amide (20) (22.3 mg) in benzene (3 ml) was refluxed for 7 h under nitrogen. Evaporation of the solvent, and chromatography of the residue on silica gel gave 2,9a-*dihydro*-9a-*dihydro*-9a-*methyl*-1H-*indeno*[1,7-cd]*azepin*-1-*one* (21) (18.4 mg, 83%) as colourless flakes, m.p. 142—143 °C (from petroleum–dichloromethane) (Found: C, 79.0; H, 5.6; N, 7.1. $C_{13}H_{11}NO$ requires C, 79.2; H, 5.6; N, 7.1%); $\nu_{max.}$ (CCl_4) 3 400, 3 220, 3 100, 2 970, 1 668, 1 642, 1 372, 1 348, 1 144, 1 054, and 848 cm^{-1}; $\lambda_{max.}$ (EtOH) 270sh (log ε 3.97), 274 (3.98), 286sh (3.86), and 345sh nm (2.11); *m/z* 197 (M^+, base), 196, 182, 178, 168, and 154.

Thermal Rearrangement of the Chlorosulphonamide (19).—(a) *In the presence of cyclohexene.* A solution of the chlorosulphonamide (19) (10.8 mg) in toluene (1.5 ml) and cyclohexene (0.5 ml) was refluxed under nitrogen for 15 min. Evaporation of the solvents, and chromatography of the residue on silica gel gave (i) the annulene (1) (2.4 mg, 42%); (ii) starting material (1.5 mg, 14% recovery); (iii) the amide (21) (2.9 mg, 40%).

(b) *In the absence of cyclohexene.* A solution of the chlorosulphonamide (19) (27.0 mg) in toluene (1 ml) was refluxed under nitrogen for 30 min. The solvent was evaporated and the residue chromatographed on silica gel. Elution with petroleum containing an increasing proportion of ether gave (i) the annulene (1) (1.6 mg, 11%); (ii) N-*chlorosulphonyl*-2,9a-*dihydro*-9a-*methyl*-1H-*indeno*[1,7-cd]-*azepin*-1-*one* (22) (6.2 mg, 23%) as an oil, $\nu_{max.}$ (CCl_4) 1 736, 1 422, 1 406, 1 044, 1 032, 910, 658, and 626 cm^{-1}; $\lambda_{max.}$ (EtOH) 254 (log ε 4.05), 275sh (3.95), 294sh (3.71), and 326sh nm (3.03); δ_H (250 MHz, $CDCl_3$) 1.49 (3 H, s, 9a-Me), 6.64 (1 H, d, *J* 9.3 Hz, 3-H or 4-H), 6.79 (1 H, d, *J* 5.8 Hz, 8-H or 9-H), 6.88 (1 H, d, *J* 5.8 Hz, 9-H or 8-H), 6.92 (1 H, d, *J* 9.3 Hz, 4-H or 3-H), 7.17 (1 H, X part of ABX system, 5-H), and 7.39 (2 H, AB part of ABX system, 6-H and 7-H); *m/z* 297—295 (1 : 3, M^+), 254—252 (1 : 3, $M^+ - CH_3 - CO$), 231, 197 (base), 196, 182, 173, and 154; (iii) starting material (3.7 mg); (iv) a 4 : 1 mixture of the amide (21) and annuleneamides (7 mg) as a yellow solid; δ_H (250 MHz, $CDCl_3$) − 1.44 and −1.46.

Birch Reduction of 7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1).—A solution of the annulene (1) (29 mg, 0.19 mmol) in dry tetrahydrofuran (3 ml) was added to a stirred solution of sodium (*ca.* 5 mg, 0.22 mg-atom) in liquid ammonia (10 ml) under nitrogen at −33 °C. The resulting orange mixture was treated with more sodium (*ca.* 5 mg, 0.22 mg-atom), and after 10 min, ammonium chloride (50 mg) was added. The resulting mixture was pale yellow. The ammonia was evaporated, and the mixture poured into water (10 ml). The products were extracted with petroleum (3 × 5 ml), and the combined extracts were dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave a pale yellow oil (22 mg). N.m.r. showed that this oil was a mixture. No products could be identified, but the mass spectrum showed ions at *m/z* 156 and 158, corresponding to dihydro- and tetrahydro- species.

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