# Pentacyclo[5,3,1,$0^{2,6}$,$0^{3,5}$,$0^{4,9}$]undecane and Tetracyclo[5,3,1,$0^{2,6}$,$0^{4,9}$]undecane

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*Summary* Direct irradiation of tricyclo[5,5,1,$0^{4,9}$]undeca-2,5-diene in ether afforded pentacyclo[5,3,1,$0^{2,6}$,$0^{3,5}$,$0^{4,9}$]-undecane which was hydrogenated to give tetracyclo-[5,3,1,$0^{2,6}$,$0^{4,9}$]undecane.

In connection with the chemistry of strained σ-bonds, bicyclo[2,1,0]pentane and its derivatives have attracted considerable attention in the past decade.[1] We now report the synthesis of pentacyclo[5,3,1,$0^{2,6}$,$0^{3,5}$,$0^{4,9}$]undecane (**1**) which includes the bicyclopentane unit in its framework as well as the tetracyclo[5,3,1,$0^{2,6}$,$0^{4,9}$]undecane (noriceane) unit (**2**).

When the stereoisomeric 2,4-dibromohomoadamantanes (**3a**) and/or (**3b**)[2] were treated with hexamethylphosphoric triamide (HMPT)[3] at 180 °C for 3 h, dehydrobromination accompaning skeletal rearrangement took place easily to give the tricyclic diene, (**4**), m.p. 155—158 °C,† in 85—90% yield: *m/e* 146 ($M^+$, 84%) and 80 (100%); $^1$H n.m.r.: δ

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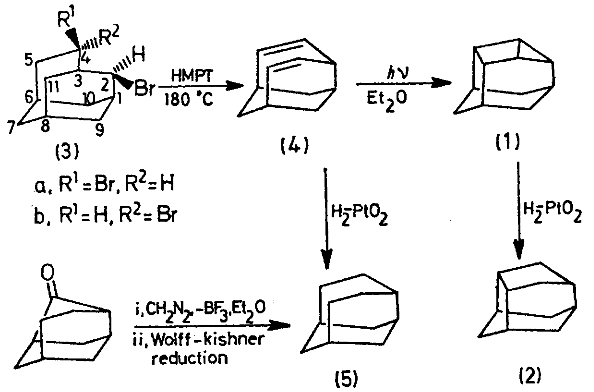
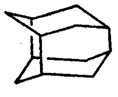
† All m.ps. were measured in sealed capillary tubes.

($CCl_4$) 0·80—3·13 (10H, br complex m) and 5·50—6·17 (4H, m); $^{13}$C n.m.r.: $\delta$ ($CDCl_3$) 137·0 (2CH=), 132·8 (2CH=), 39·4 ($2CH_2$), 38·2 (CH), 32·2 (2CH), 26·9 (CH), and 24·0 ($CH_2$).





(6)

The skeletal structure of (**4**) was further supported by the fact that hydrogenation of (**4**) over $PtO_2$ gave the saturated hydrocarbon (**5**) [*m/e* 150 ($M^+$, 100%); $^1$H n.m.r.: $\delta$ ($CCl_4$) 0·90—3·10 (18H, br complex m); $^{13}$C n.m.r.: $\delta$ ($CDCl_3$) 41·4 ($CH_2$), 31·3 ($2CH_2$), 30·1 ($2CH_2$), 28·1 ($2CH_2$), 26·6 (2CH), 26·5 (CCH), and 25·3 (CH)] which was identical ($^1$H n.m.r.) with authentic tricyclo[5,3,1,0$^{4,9}$] undecane, m.p. 242—246 °C, which was prepared from 2-protoadamantanone by ring enlargement using $CH_2N_2$ (catalysed by $BF_3$–$EtO_2$)[4] followed by Wolff–Kishner reduction of the resulting ketone.‡

Direct irradiation of (**4**) in ether with quartz-filtered light for 18 h induced an intramolecular [2+2]cycloaddition[5] to afford the saturated compound (**1**), m.p. 183—186 °C, as the sole product in 85% yield. Compound (**1**) in $CCl_4$ showed an i.r. band at 3100 cm$^{-1}$ indicative of a cyclopropane ring. Other spectral data are also compatible with structure (**1**) [*m/e* 146 ($M^+$, 52%) and 80 (100%); $^1$H n.m.r.: $\delta$ ($CCl_4$) 0·50—2·90 (14H, complex m); $^{13}$C n.m.r.: $\delta$ ($CDCl_3$) 43·3 ($CH_2$), 38·3 (2CH), 33·1 ($2CH_2$), 30·3 (2CH), 22·5 (CH), 20·0 (CH), and 7·3 (2CH)].

When (**1**) was hydrogenated over $PtO_2$ in MeOH, 1 mol. equiv. of hydrogen was absorbed to give compound (**2**),§ m.p. 212—215 °C [*m/e* 148 ($M^+$, 100%); $^1$H n.m.r.: $\delta$ ($CCl_4$) 0·60—2·67 (16H, br complex m); $^{13}$C n.m.r.: $\delta$ ($CDCl_3$) 41·9 (2CH), 40·9 ($CH_2$), 38·1 (2CH), 33·7 (CH), 30·9 ($2CH_2$), 30·5 (CH), and 29·5 ($2CH_2$)]. The disappearance of the i.r. band at 3100 cm$^{-1}$ also indicated cleavage of the cyclopropane ring. This hydrogenation is in good agreement with the well known fact that cleavage of the central bond of bicyclo-[2,1,0]pentane ring system occurs easily in a number of reactions.[6]

The $^{13}$C n.m.r. data are conclusive in determining the structures of (**1**), (**2**), (**4**), and (**5**), all of which have a mirror plane.

The fixed bicyclopentane ring in the cage structure is interesting in that any attacking species must approach the bicyclopentane unit from the *exo* side alone and, in addition, isomerization to a cyclopentene derivative is impeded on the stereochemical grounds (*e.g.* Bredt's rule[7]).

(*Received*, 6*th June* 1975; *Com.* 639.)

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‡ This ketone gave satisfactory elemental analysis and consistent i.r., $^1$H n.m.r., and mass spectra. However, the position of carbonyl function has not been determined yet.

§ Compound (**2**) could be named noriceane. For iceane (**6**), see C. A. Cupas and L. Hodakowski, *J. Amer. Chem. Soc.*, 1974, **96**, 4668; D. P. G. Hamon and G. F. Taylor, *Tetrahedron Letters*, **1975**, 155.

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