auf *ca.* – 10° abgekühlt, diese hierauf auf – 10° gekühlte 40proz. Natronlauge gegossen (*ca.* 200 ml). Dabei erhöht sich die Temperatur auf 20°. Es entsteht eine braun-rote milchige Emulsion, die während etwa 3 Min. gerührt wird. Dann 4mal mit je 100 ml peroxidfreiem Äther ausschütteln. Die vereinigten Ätherphasen werden nochmals mit 100 ml Wasser ausgeschüttelt und über Na_2SO_4 getrocknet.

Wegen der Wärmeempfindlichkeit des Produktes müssen die Destillationen bei tiefer Temperatur im Vakuum durchgeführt werden. Die Abtrennung des Äthers erfolgt im Wasserstrahlvakuum, wobei sowohl Destillationskolben als auch Vorlage mit CO_2/2-Propanol gekühlt werden. Es ist jedoch unvermeidlich, dass etwas Substanz mit dem Äther übergeht.

Der Rückstand wird im Hochvakuum (*ca.* 0,2 Torr) destilliert, indem die Vorlage weiterhin mit CO_2/2-Propanol gekühlt wird. Das Thietan geht als farblose Flüssigkeit über, anfangs sehr rein, später gelegentlich verunreinigt mit einigen Prozenten Dihalid (GC.). Sdp. *ca.* 115°/760 Torr (Zers.) (nach [2] 112,5°), Ausbeute 90%. Das Produkt wurde anhand von NMR. und MS. identifiziert (siehe Text).

Den Herren Dres. *H. P. Kriemler* und *H. Sauter* sei an dieser Stelle für die Aufnahme und Interpretation der Massen- bzw. NMR.-Spektren herzlich gedankt.

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274. 3-Oxawurtzitane (3-Oxatetracyclo[5.3.1.1^{2,6}0^{4,9}]dodecane)

by **Rolf Otto Klaus, Hans Tobler,** and **Camille Ganter**

Laboratorium für Organische Chemie der Eidg. Technischen Hochschule, CH–8006 Zürich

(25. X. 74)

Summary. A synthesis of 3-oxawurtzitane (3-oxatetracyclo[5.3.1.1^{2,6}0^{4,9}]dodecane) (**8**) is described.

In connection with our studies on bridged polycyclic heterocompounds[1] we here describe a synthesis of 3-oxawurtzitane[2] (3-oxatetracyclo[5.3.1.1^{2,6}0^{4,9}]dodecane) (**8**), the first heterocyclic member with this skeleton.

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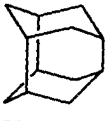
[1] See [1] and earlier papers on heterotricyclodecanes.

[2] For the carbocyclic analog **1**, recently synthesized by *Cupas & Hodakowski* [2], the trivial name '*iceane*' was proposed on the ground that 'this molecule is geometrically the hydrocarbon

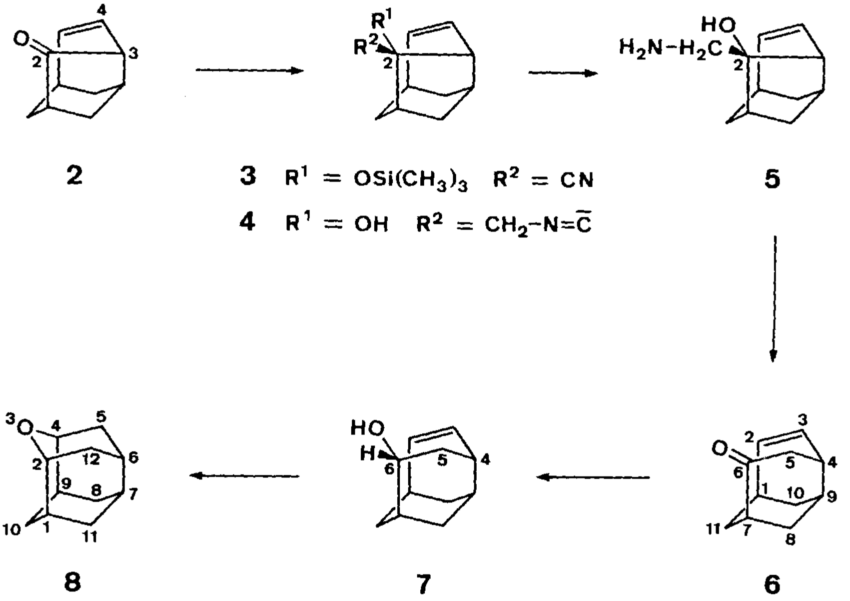


1

analog of crystalline water' [2] [3]. However, since the carbon skeleton of **1** is more accurately described as being isostructural with a portion of the wurtzite structure, we prefer the trivial name '*wurtzitane*', especially since its translation into other languages presents no difficulties, in contrast to 'iceane'.

As starting material we used tricyclo[4.3.1.$0^{3,8}$]dec-4-en-2-one (protoadamant-4-en-2-one) (**2**) which is conveniently prepared by pyrolysis of 7-allyloxycycloheptatriene [4]. The main synthetic problem was to introduce one more carbon atom between C(2) and C(3) in **2**. This was achieved by a *Tiffeneau-Demjanov* ring expansion [5] of the β-amino-alcohol **5**, obtained by two separate routes: Treatment of protoadamant-4-en-2-one (**2**) with trimethylsilylcyanide at room temperature [6] yielded almost quantitatively the cyanotrimethylsilyloxy compound **3**³) [IR. (neat): 2225, 1255, 845, 754; NMR. ($CDCl_3$): 0.25/*s*, $(H_3C)_3$-Si-O-C(2)]. Reduction of **3** with $LiAlH_4$ in ether gave the β-amino-alcohol **5**, which was characterized as its hydrochloride **5**-HCl [75% yield; m.p. 223–225°; IR. (KBr): 3450, 1593].

Reaction of ketone **2** with isocyanomethyllithium in tetrahydrofuran [7] yielded almost quantitatively the isocyanomethyl-protoadamantenol **4** [IR. (CCl_4): 3550, 2155; NMR. ($CDCl_3$): 3.58/*m* ($W^1/_2$ approx. 5), $\bar{C}$=N-CH_2-C(2)], which was transformed to the hydrochloride **5**-HCl of the desired β-amino-alcohol **5** by methanolysis (CH_3OH/HCl) in 80% yield.



Ring expansion was accomplished by treatment of **5**-HCl with sodium nitrite in aqueous acetic acid (*Tiffeneau-Demjanov* conditions [5] [7]). The only new ketone formed was tricyclo[5.3.1.$0^{4,9}$]undec-2-en-6-one (**6**) [90% yield; m.p. 260–262°; IR. (CCl_4): 1730]. Strong evidence for the location of the ketone function at C(6) rather than at C(5) was obtained from the NMR. spectrum (CCl_4) of the corresponding alcohol **7** (m.p. 290–292°), the product of the quantitative $LiAlH_4$-reduction of the ketone **6**. Spinspin decoupling experiments between H–C(4) (δ 2.62) and H–C(6)

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³) **3** and all the compounds described hereafter gave satisfactory elemental analyses; all m.p. are uncorrected; IR.: ν_{max} in cm^{-1}; NMR.: chemical shifts are reported in δ units relative to internal TMS, δ 0.00 ppm, coupling constants are given in Hz.

(δ 3.98) showed $J_{4,6} \leq 0.5$ Hz. If the hydroxyl group were located at C(5) a larger coupling constant ($J_{4,5}$) would be expected.

The above assignments were verified by the successful ring closure of alcohol **7** to 3-oxawurtzitane (**8**). Hydroxymercuration of **7** with mercuric acetate in water, followed by $NaBH_4$-reduction in aqueous sodium hydroxide solution, gave **8** in 80% yield with respect to reacted starting material (60% isolated material). The intramolecular ether formation was also accomplished in lower yields with sulfuric acid in benzene or ether solutions. 3-Oxawurtzitane (**8**), m.p. 312–313° shows the following spectral properties: IR. (CCl_4): 1029; ^{1}H-NMR. ($CDCl_3$): 2.33/*m*, H–C(1) and –C(9); 4.24/*m*, H–C(2) and –C(4), $J_{1,2} = J_{4,9} = 10$ Hz (determined by double irradiation experiments); ^{13}C–NMR. ($CDCl_3$): only seven lines due to the symmetry plane through O(3), C(7) and C(10) δ 69.7 (2 C); 31.2 (2 C); 31.2 (2 C); 29.8 (2 C); 28.0 (1C); 27.8 (1 C); 24.2 (1 C).

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275. Selective Population of the n,π^* and π,π^* Triplet States of 1-Indanones

by **Walter Amrein, Inga-Mai Larsson,** and **Kurt Schaffner**
Département de Chimie Organique, Université de Genève, 1211 Genève 4

(11. X. 74)

Summary. The two components of the dual phosphorescence of 1-indanone (**1**) and six related ketones (**2–7**) possess different excitation spectra exhibiting the vibrational progression characteristic of the $S_0 \rightarrow S_1$ (n, π^*) transition (shorter-lived emission) and two bands of the $S_0 \rightarrow S_{2 \text{ and } 3}$ (π, π^*) 0–0 transitions, respectively. The most favorable intersystem crossing routes are S_1 (n, π^*) $\rightarrow$ T (n, π^*) and $S_{2,3}$ (π, π^*) $\rightarrow$ T (π, π^*). Internal conversion to S_1 competes more effectively with S (π, π^*) $\rightarrow$ T (π, π^*) intersystem crossing only from higher vibrational levels of the S_2 and S_3 states.

In the course of a stereochemical study of the intramolecular electronic energy transfer in bridged compounds with conformationally rigid orientations of 2,3-indanono and naphtho chromophores [1] we have investigated some of the luminescence properties of the hexahydrofluorenone **2** and the bridged analogues **3–7** in ether/isopentane/ethanol 5:5:2 (EPA) at 77K. Like the parent ketone 1-indanone (**1**) these six compounds do not fluoresce at room temperature owing to near-unity