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Synthesis of Novel Tricyclononanes

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Abstract: Hitherto unknown tricyclo[4.2.1.$0^{3,8}$]nonan-5-one (**2**) was prepared by reductive cleavage of tetracyclo[3.3.1.$0^{2,8}$.$0^{3,7}$]nonan-9-one (**1**) with lithium in liquid ammonia or reducting **1** *via* photochemically induced electron transfer. Tricyclic ketone **2** served as precursor for the synthesis of two novel hydrocarbons, i. e. tricyclo[4.2.1.$0^{3,8}$]nonane (**3**) and tricyclo[4.2.1.$0^{3,8}$]non-4-ene (**5**).

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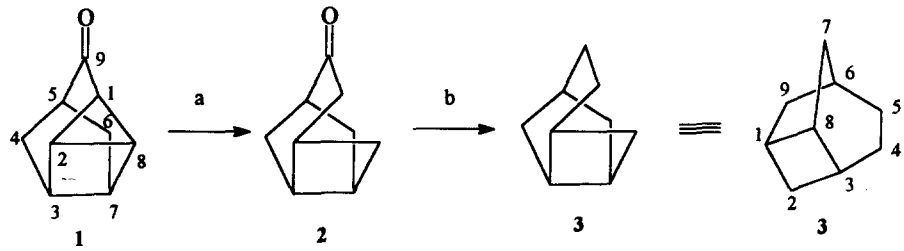
Cyclopropyl ketones undergo cleavage of the cyclopropane ring when reduced with lithium in liquid ammonia.[1] It has been found that the reaction is controlled by the overall steric configuration of the molecule, i. e. the cyclopropane ring C-C bond which better overlaps the π-bond of the adjacent unsaturated center is the bond which is preferentially cleaved reductively. Reductive cleavage of cyclopropyl ketones by samarium(II) iodide,[2] and by photochemically induced electron transfer[3] has been reported recently as well.

As part of our continuing interest in the synthesis and chemistry of polycyclic molecules,[4,5] with the above concept in mind, single electron transfer induced ring opening reactions of cyclopropyl ketone **1** were employed to obtain hitherto unknown tricyclo[4.2.1.$0^{3,8}$]nonan-5-one (**2**). Tricyclic ketone **2** served as precursor for the synthesis of two novel hydrocarbons **3** and **5**, (Schemes I and II).

The synthesis of tetracyclo[3.3.1.$0^{2,8}$.$0^{3,7}$]nonan-9-one (**1**) is readily performed by starting with 4-brenden-2-one,[4] which could be converted photochemically into **1** in 25% isolated yield.[5]

Scheme I



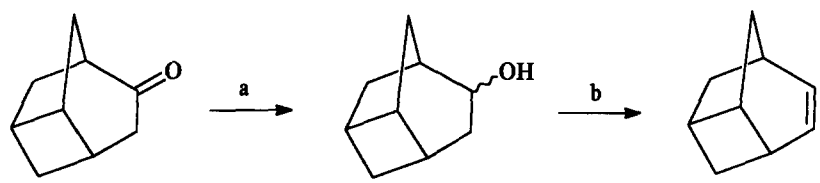
1 2 3 3

a) Li/NH_3 or $h\nu/Et_3N/LiClO_4/CH_3CN$
b) H_2NNH_2/KOH/diethylene glycol

Subsequent treatment of **1** with Li/NH_3 produced a single ketone (26% yield) to which we have assigned the structure tricyclo[4.2.1.$0^{3,8}$]non-5-one (**2**). However, irradiation of ketone **1** at 254 nm in CH_3CN in the presence of $LiClO_4$ (1 equivalent) and Et_3N (10 equivalents) afforded tricyclic ketone **2** in 56% of yield. Wolf-Kishner reduction of ketone **2** gave tricyclo[4.2.1.$0^{3,8}$]nonane (**3**, 53%) which belongs to the family of noradamantane isomers of the formula C_9H_{14}.

Tricyclic ketone **2** also served as a precursor for the preparation of tricyclo[4.2.1.$0^{3,8}$]nonane derivatives,[6] e. g., tricyclo[4.2.1.$0^{3,8}$]nonan-5-ol (**4**) and tricyclo[4.2.1.$0^{3,8}$]non-4-ene (**5**) (Scheme II).

Scheme II



2 *endo*-**4** and *exo*-**4** (92 : 8) **5**

a) $LiAlH_4$/diethyl ether
b) HMPA, 230 °C

In order to prepare **4** and **5**, tricyclic ketone **2** was first reduced with $LiAlH_4$ to give 70% yield of **4** as a mixture of *endo*- and *exo*- stereoisomers (product ratio 92:8).[7] Subsequent dehydratation of **4** with HMPA at 230 °C afforded **5** as the sole product.[8]

In summary, the synthetic approach described above provides a straightforward entry into the tricyclo[4.2.1.$0^{3,8}$]nonane skeleton and various derivatives. We are continuing to explore the chemistry of **1** and related derivatives. Further studies on the interconversion of **1** to the tricyclo[4.2.1.$0^{3,8}$]nonane skeleton are in progress.

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6. To the best of our knowledge, the only examples published to date include the preparation of some polyfunctionalized tricyclo[4.2.1.$0^{3,8}$]nonane skeleta in a protracting syntheses or as a mixture of products (a) by intramolecular photochemical [2+2] cycloadditions : Fröstl, W.; Margaretha, P. *Helv. Chim. Acta.* **1976**, *59*, 2244-2248. Martin, S. F.; White J. B. *Tetrahedron Lett.* **1982**, *23*, 23-26.; Cruciani, G.; Margaretha P. *Helv. Chim. Acta* **1990**, *73*, 288-296.; McMurry, T. B. H.; Work, A.; McKenna, B. *J. Chem. Soc., Perkin Trans. I*, **1991**, 811-816; (b) by tandem intramolecular Michael-aldol reactions: Ihara, M.; Ohnishi, M.; Takano, M.; Makita, K.; Taniguchi, N.; Fukumoto, K. *J. Am. Chem. Soc.* **1992**,

114, 4408-4410.; Ihara, M.; Taniguchi, T.; Makita, K.; Takano, M.; Ohnishi, M.; Taniguchi, N.; Fukumoto, K.; Kabuto, C. *J. Am. Chem. Soc.* **1993**, *115*, 8107-8115 and (c) by solvolysis of tricyclo[3.2.1.$0^{3,6}$]octan-1-ylmethyl toluene-*p*-sulphonate: Luh, T-Y.; Lei, K. L. *J. Chem. Soc., Chem. Commun.* **1981**, 214-215.

7. The ratio of *endo*-**4** to *exo*-**4** was determined by careful integration of the ^{1}H NMR spectrum of the mixture of isomers.
8. Satisfactory elemental analyses and/or exact mass molecular weights have been obtained for all new compounds shown.

   (a) Spectroscopic data for **2**: IR (KBr): ν = 2940 cm^{-1} (s), 2850 (m), 1720 (s, C=O); ^{1}H NMR ($CDCl_3$): δ 1.07 (m, 1 H), 1.56 (ddd, *J* = 12.9, 4.2, 4.2 Hz, 1 H), 1.69 (d, *J* = 13.2 Hz, 1 H), 1.92-1.98 (m, 2 H), 2.18 (d, *J* = 17.0 Hz, 1 H), 2.47 (ddd, *J* = 17.0, 5.0, 2.4 Hz, 1 H), 2.53-2.69 (m, 3 H), 2.87 (m, 1 H), 3.11 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ = 26.8 (d), 30.7 (t), 33.4 (t), 34.7 (d), 36.5 (d), 38.1 (t), 40.4 (t), 52.4 (d), 217.2 (s).

   (b) Spectroscopic data for **3**: ^{1}H NMR ($CDCl_3$) δ = 1.10 (ddd, *J* = 12.1, 4.8, 4.8 Hz, 1 H), 1.20-1.32 (m, 3 H), 1.45-1.77 (m, 4 H), 1.97 (m, 1 H), 2.25 (ddd, *J* = 9.8, 5.3, 5.3 Hz, 1 H), 2.33-2.45 (m, 2 H), 2.55 (m, 1 H), 2.72 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ = 20.9 (t), 27.5 (t), 30.5 (t), 31.0 (t), 31.5 (d), 34.2 (d), 35.0 (d), 37.8 (d), 41.6 (t).

   (c) Spectroscopic data for mixture of *endo*-**4** and *exo*-**4**: ^{1}H NMR ($CDCl_3$) δ = 1.20-1.55 (m), 1.82-1.92 (m), 1.98 (d, *J* = 13.5 Hz), 2.16-2.20 (m), 2.35-2.47 (m), 2.50-2.60 (m), 2.71-2.77 (m), 4.06 (dd, *J* = 8.1, 7.9 Hz, H-COH of *exo*-**4**), 4.38 (dd, *J* = 7.6, 7.6 Hz, H-COH of *endo*-**4**). ^{13}C NMR of *endo*-**4** ($CDCl_3$) δ = 30.6 (t), 31.1 (t), 31.2 (d), 31.7 (t), 32.4 (t), 34.4 (d), 36.3 (d), 41.4 (d), 70.2 (d). ^{13}C NMR of *exo*-**4** ($CDCl_3$) δ = 28.1 (t), 28.6 (d), 30.9 (t), 32.0 (t), 34.8 (d), 37.0 (d), 38.4 (t), 45.3 (d), 73.2 (d).

   (d) Spectroscopic data for **5**: ^{1}H NMR ($CDCl_3$) δ = 1.23 (d, *J* = 10.4 Hz, 1 H), 1.27 (d, *J* = 11.8 Hz, 1 H), 1.48 (ddd, *J* = 11.3, 4.2, 3.7 Hz, 1 H), 1.59 (d, *J* = 12.5 Hz, 1 H), 1.74 (ddd, *J* = 12.5, 8.7, 5.6 Hz, 1 H), 2.45-2.70 (m, 4 H), 3.00 (m, 1 H), 5.88 (dd, *J* = 8.8, 6.2 Hz, 1 H), 6.32 (dd, *J* = 8.4, 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ = 34.3 (d), 35.9 (t, 2 C), 37.3 (d), 37.9 (d), 38.5 (d), 40.2 (t), 131.9 (d), 137.4 (d).

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