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THE ISOMERIC BIADAMANTYLKETIMINES

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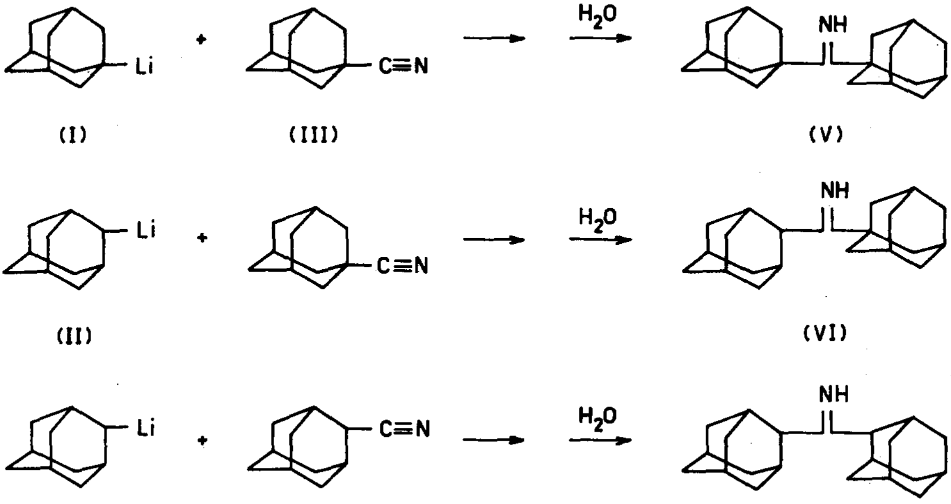
The stabilizing effect of the adamantyl moiety has led to the preparation of compounds which until recently have only been postulated as intermediates[1,2] or were known in the literature as unstable.[3]

We now wish to report another example of the significant stabilizing effect of adamantyl groups. We synthesized the three biadamantylketimines V, VI and VII by allowing lithioadamantanes to react with cyanoadamantanes and found the ketimines to have a remarkable resistance to hydrolysis. This was demonstrated by the fact that they could be isolated from the reaction mixtures by salt formation.



(I) (III) (V)

(II) (VI)

(IV) (VII)

The reactions were carried out at -60° in ether solutions. The lithioadamantanes were prepared first in situ by standard procedures[4,5], followed by addition of equimolar amounts of the appropriate cyanoadamantane.[6]

In addition to the mentioned biadamantylketimines, corresponding t-butyladamantylketimines and biadamantyls were also formed in appreciable yields as a consequence of the exchange reaction used. The yields of products are given in table I.

Table I

substrates	biad.ketimine	yield %[+]	t-butyl-ad.ketimine %[+]	biadamantyl %[x]
I + III	V	30	44	70
II + III	VI	43	45	56
II + IV	VII	55	40	45

[+] yield based on consumed cyanoadamantane.

[x] yield based on consumed iodoadamantane.

The mixture of biadamantyl- and t-butyl-adamantylketimine was separated from the biadamantyl and unreacted cyanoadamantane by treating the mixture with hydrochloric acid and extracting the aqueous layer with hexane. The acid solution (containing the ketimine HCl-salts) was neutralized and extracted with ether. After drying and evaporating the solvent, the ketimine mixture remained. The biadamantylketimine could be obtained in pure form from this mixture by crystallization from methanol at -30°.

Spectral properties and melting ranges:

1,1'-biadamantylketimine (V): m.p. 113.5-116.1° (corr.)

IR-spectrum (KBr): 3160 cm^{-1} (very weak, sharp) N-H str., 1592 cm^{-1} (strong) C=N str.

NMR-spectrum (CCl_4): $\tau = 7.93$ (18H) and $\tau = 8.25$ (12H) unresolved multiplets, $\tau = 1$ (1H) (broad) N-H.

Mass spectrum: M^+ at m/e 297 $(C_{21}H_{31}N)^+$, $M-C_{10}H_{15}$ at m/e 162, $M-C_{11}H_{16}N$ at m/e 135.

1,2-biadamantylketimine (VI): m.p. 148-155° (corr.)

IR-spectrum (KBr): 3220 and 3260 cm^{-1} (very weak, sharp) N-H str., 1620 cm^{-1} (strong) C=N str.

NMR-spectrum (CCl_4): $\tau = 7.23$ (1H) and $\tau = 7.35$-8.86 (29H) multiple absorptions, $\tau = 1$ (1H) (broad) N-H.

Mass spectrum: identical to that of V.

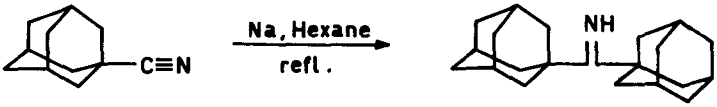
2,2'-biadamantylketimine (VII): m.p. 134-143° (corr.)

IR-spectrum (KBr): 3280 cm^{-1} (weak, sharp) N-H str., 1630 cm^{-1} (strong) C=N str.

NMR-spectrum (CCl_4): τ = 7.63 (2H) and τ = 7.70-8.80 (28H) complex multiplets, τ = 1 (1H) (broad) N-H.

Mass spectrum: M^+ at m/e 297 $(C_{21}H_{31}N)^+$, $M-C_{10}H_{16}$ at m/e 161.

Compound V was also prepared in an excellent yield by employing the method used by Harzler for the preparation of the stable di-t-butylketimine.[7]

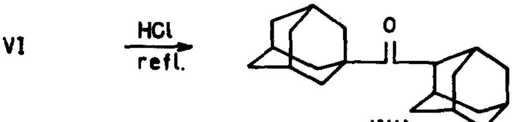


(III) (V)

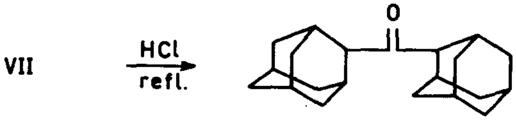
Refluxing 1-cyanoadamantane (III) with excess of dispersed sodium in hexane for seven hours gave the ketimine in a 90% yield. It was purified by the salt formation procedure outlined above. A similar reaction, applied to 2-cyanoadamantane (IV) to obtain VII had no success, even by heating the starting.material with dispersed sodium in heptane.

In order to get the ketones corresponding to the ketimines, we carried out short hydrolyses in diluted hydrochloric acid. Samples of the pure ketimines (50 mgr.) were introduced into

(VIII)



(IX)



(X)

refluxing solutions of 5N hydrochloric acid (30 ml) for 30 minutes, followed by quick cooling to room temperature. As determined by VPC 2,2'-biadamantylketimine (VII) proved to be by far the most resistant towards hydrolysis (only 5% conversion), followed by 1,2'-biadamantylketimine (VI) with 26% and finally 1,1'-biadamantylketimine (V) with 66% conversion.

Though no quantitative data have been collected, it is clear from these results that tertiary and secondary attached adamantane moieties exert quite different influences, which may be regarded as a combination of steric and inductive effects.

Complete hydrolysis of the three ketimines was effected by prolonged reflux in 5N hydrochloric acid (up to fifteen hours). Nearly quantitative conversion to the corresponding ketones VIII, IX and X[4] occurred. Analytical pure samples of VIII and IX were obtained by crystallization from methanol.

Spectroscopic properties and melting ranges:

1,1'-biadamantylketone (VIII): m.p. 185.6-186.0° (corr.).
IR-spectrum (KBr): C=O str. at 1675 cm^{-1}
NMR-spectrum (CCl_4): $\tau = 7.97$ (18H) and $\tau = 8.25$ (12H) unresolved multiplets.
Mass spectrum: M^+ at m/e 298 $(C_{21}H_{30}O)^+$, $M-C_{10}H_{15}$ at m/e 162, $M-C_{11}H_{15}$ at m/e 135.

1,2'-biadamantylketone (IX): m.p. 180.1-180.5° (corr.).
IR-spectrum (KBr): C=O str. at 1695 cm^{-1}
NMR-spectrum (CCl_4): $\tau = 6.87$ (1H) and $\tau = 7.66$-8.60 (29H) complex multiplets.
Mass spectrum: M^+ at m/e 298 $(C_{21}H_{30}O)^+$, $M-C_{10}H_{15}$ at m/e 162, $M-C_{11}H_{15}O$ at m/e 135.

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4. J.H. Wieringa, H. Wynberg and J. Strating, Synth. Comm., 1, 7 (1971).
5. J.H. Wieringa, J. Strating and H. Wynberg, Synth. Comm., in press.
6. The cyanoadamantanes were prepared by standard procedures from the corresponding carboxylic acids. They were purified by chromatography on aluminium oxide. Melting points: 1-cyanoadamantane: 194.6-195.1° (corr.); 2-cyanoadamantane: 181-182° (uncorr.).
   We thank Drs. S. Reiffers for his gift of 2-cyanoadamantane.
7. H.D. Harzler, J. Amer. Chem. Soc., 93, 4527 (1971).