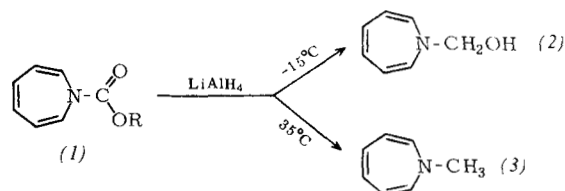


## Dimerization of 1-Methylazepine

By Prof. K. Hafner and J. Mondt<sup>[1]</sup>

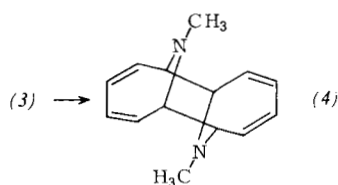
Institut für Organische Chemie, Universität München, and Technische Hochschule Darmstadt (Germany)

The preparation of alkyl 1-azepinecarboxylates (1) by photolysis or thermolysis of azidoformates in benzene or its derivatives has enabled us to study the monocyclic azepine system<sup>[2]</sup>. On reduction of (1), R=C<sub>2</sub>H<sub>5</sub>, with LiAlH<sub>4</sub> in ether at -15°C we obtained 1-azepinemethanol (2)<sup>[3]</sup> in ca. 45% yield as a thermally unstable, pale yellow oil



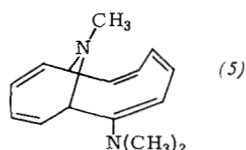
[UV spectrum (in *n*-hexane):  $\lambda_{\text{max}} = 232 \text{ m}\mu$ , shoulder at  $255 \text{ m}\mu$ ], which was isolated as picrate (decomp. > 100°C)<sup>[4]</sup>. In boiling ether the same reduction leads to 1-methylazepine (3)<sup>[3]</sup> in 60% yield as a thermally rather unstable, yellow oil [b.p. 20°C/10<sup>-3</sup> mm; structureless UV spectrum, with  $\epsilon$  rising towards shorter wavelengths and  $\lambda_{\text{max}} = 236 \text{ m}\mu$  ( $\epsilon = 5100$ ) with shoulders at  $249 \text{ m}\mu$  ( $\epsilon = 4020$ ),  $258 (3660)$ ,  $288 (1950)$ , and  $384 (65)$  (in *n*-hexane); NMR spectrum (in CCl<sub>4</sub>), singlet at  $7.55 \tau$  (CH<sub>3</sub>), multiplet at  $5.0$  to  $5.5 \tau$  (6 ring protons)]. Catalytic hydrogenation (Raney Ni; 20°C) of the azepine (3) leads to hexahydro-1-methylazepine<sup>[5]</sup>.

The azepine (3) dimerizes rapidly in ether above 0°C, yielding the colorless 13,14-dimethyl-13,14-diazatricyclo-[6.4.1.12.7]tetradeca-3,5,9,11-tetraene (4), m.p. 171°C,  $\lambda_{\text{max}}$  (in *n*-hexane) =  $230 \text{ m}\mu$  ( $\epsilon = 15680$ ),  $237.5 (16600)$ , and was purified by chromatography with ether on Al<sub>2</sub>O<sub>3</sub> and recrystallization from methanol<sup>[6]</sup>. The structure of this dimer follows from the NMR spectrum (in CDCl<sub>3</sub>), which shows a singlet for the 6 methyl protons at  $7.8 \tau$ , a doublet for the 4 bridgehead protons at  $6.7 \tau$ , and a multiplet for the 8 olefinic protons centered at  $4.1 \tau$ . The dipole moment of the dimer is 0.5 D, which indicates the *trans*-form for (4)<sup>[7]</sup>. The mass spectrum<sup>[8]</sup> confirms the molecular weight (214); the signal of greatest intensity is at *m/e* 107, which indicates preferential decomposition of (4) to the monomer (3); the lower *m/e* values form a pattern characteristic for further decomposition of (3). On catalytic hydrogenation, the dimer (4) takes up the amount of H<sub>2</sub> calculated for 4 double bonds<sup>[8a]</sup>.



We suggest that dimerization of (3) occurs in several stages. 1,3-Dipolar addition of (3), which can be formulated as an azomethine ylide, is improbable in view of the rules of Woodward and Hoffmann<sup>[9]</sup>.

With hydrogen bromide, the dimer (4) gives a dihydrobromide (colorless leaflets, decomp. 240°C), but with styphnic or picric acid it gives only the monoprotonated product



(styphnate, decomp. 196°C; picrate, decomp. 195°C). With methyl iodide in boiling methanol (60 hr) it gives a mono-methiodide (decomp. 195°C), which is converted by Hofmann degradation into the cyclododecapentaene derivative (5), which forms a yellow oil with  $\lambda_{\text{max}}$  (in *n*-hexane) =  $249.5 \text{ m}\mu$ ; NMR spectrum (in CCl<sub>4</sub>): two singlets at  $7.6$  and  $7.8 \tau$  (3 CH<sub>3</sub>), a multiplet centered at  $7.15 \tau$  (2 bridgehead protons), and a multiplet centered at  $4.15 \tau$  (9 olefinic ring protons).

Received: July 4th, 1966; revised July 17th, 1966 [Z 295 IE]  
 German version: Angew. Chem. 78, 822 (1966)

[1] Diploma Thesis, Universität München, 1965.

[2] K. Hafner and C. König, Angew. Chem. 75, 89 (1963); Angew. Chem. internat. Edit. 2, 96 (1963); K. Hafner, Angew. Chem. 75, 1041 (1963); Angew. Chem. internat. Edit. 3, 165 (1964); K. Hafner, D. Zinser and K. L. Moritz, Tetrahedron Letters 1964, 1733.

[3] There are indications that (2) and (3) are in equilibrium with small amounts of the valence-isomeric 1,2-epimino-1,2-dihydrobenzene derivatives. Aromatization of (3) to *N*-methylaniline was observed alongside the dimerization.

[4] Satisfactory analytical results were obtained for all the new compounds.

[5] R. Lukes and J. Malek, Coll. Czechoslov. chem. Commun. 16, 23 (1951).

[6] Analogous dimerization of (1) and 1-cyanoazepine, but only at 200°C, has recently been reported by L. A. Paquette and I. H. Barrett, as well as by A. L. Johnson and H. E. Simmons, J. Amer. chem. Soc. 88, 2590 (1966).

[7] An X-ray structure analysis of (4) is in progress.

[8] We thank Prof. G. Spiteller, Göttingen, for measurement and discussion of the mass spectrum of (4).

[8a] Note added in proof: We have recently isolated a further dimer of (3), but its structure is not yet known. This compound forms colorless crystals and melts at 66°C; UV spectrum (in methanol):  $\lambda_{\text{max}} = 242 \text{ m}\mu$  ( $\epsilon = 4470$ ). NMR spectrum in CCl<sub>4</sub>: 2 singlets at  $7.15$  and  $7.8 \tau$  (2 (CH<sub>3</sub>)), multiplets centered at  $6.35 \tau$  (4 H) and  $4.3 \tau$  (8 H).

[9] R. Hoffmann and R. B. Woodward, J. Amer. chem. Soc. 87, 4388 (1965), and earlier papers.

## Transport Reactions of Silicides and Borides of Transition Metals

By Dr. J. Nickl, M. Duck, and J. Pieritz

Forschungslaboratorium für Festkörperchemie, Institut für anorganische Chemie, Universität München (Germany)

We have grown single crystals of silicides and borides by chemical transport reactions. The transport vessels used were silica ampoules (10 mm in diameter, 100 mm in length) in which the starting material was placed at the hot end. The reagents were the elements in massive form or powdered silicides or borides. Chlorine, bromine, or iodine at a pressure of 5 to 120 mm Hg and 20°C served as gases for both reaction and transport. Before addition of the halogen the ampoules containing the starting material were heated at 10<sup>-4</sup> to 10<sup>-5</sup> mm; the ampoules were sealed off at a pressure of ca. 10<sup>-5</sup> mm in an oxyhydrogen flame. The time for transport was 2 to 22 days. The crystals (volume several mm<sup>3</sup>) obtained were investigated by stereography and X-ray diffraction and finally their stoichiometry was determined by analysis.

The following compounds were found as well-formed single crystals at the cool end of the tubes: TiSi<sub>2</sub>, VSi<sub>2</sub>, CrSi<sub>2</sub>, Cr<sub>3</sub>Si, NbSi<sub>2</sub>, TaSi<sub>2</sub>, TiB<sub>2</sub>, VB<sub>2</sub>, CrB<sub>2</sub>, CrB, and ZrB<sub>2</sub>. However, silicides were not obtained from Zr (ZrSi<sub>2</sub> - this and other entries in parentheses are starting materials), W (W + Si, WSi<sub>2</sub>), U (U + Si), and no boride from Nb (NbB), Hf (HfB<sub>2</sub>), Ta (TaB), or W (WB); in these cases only well-crystallized silicon was formed at the cool end from silicides, and no transport was observable from borides.