symmetrical spectrum contains five pairs of lines (distances from the centre: 901, 1414, 1591, 1613, 1922 Hz; TMS at 276 Hz).

[*] Dr. H. Spiesecke and Mlle. J. Bellion-Jourdan
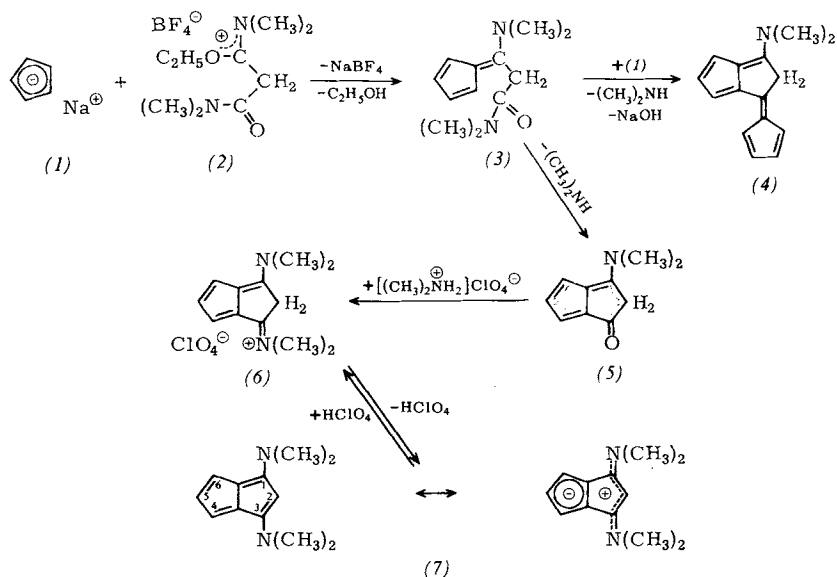Euratom Research Center, Magnetic Resonance
Ispra (Italy)

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1,3-Bis(dimethylamino)pentalene

By *K. Hafner*, *K. F. Bangert*, and *V. Orfanos* [*]

Hitherto it has not been possible to synthesize pentalene or its simple derivatives [1]. Like fulvene, pentalene should be stabilized by electron donors in the 1- or 3-position [2]. Synthesis of the thermally stable 1,3-bis(dimethylamino)-pentalene (7) has now confirmed this hypothesis.

Cyclopentadienylsodium (1) in tetrahydrofuran reacts at 20 °C with the complex (2) (a yellow, viscous oil) obtained from tetra-N-methylmalonodiamide and triethyloxonium tetrafluoroborate, yielding the fulvene derivative (3) {yield

affords the immonium perchlorate (6) (yield 95 %) as yellow needles (from CH_3CN), decomp. > 150 °C, λ_{max} = 253 mμ (log ε = 4.47), 260 (4.48), 359 (4.11), 3.97 (4.30) in CH_3CN, NMR spectrum (in [D_6]dimethyl sulfoxide) 3 singlets at τ = 3.04 (3 olefinic ring protons), 5.43 (CH_2), and 6.50 [2 $N(CH_3)_2$].

Deprotonation of (6) by a strong base (e.g. isopropylmagnesium chloride) in ether leads to compound (7), which is purified by sublimation in a high vacuum at 110 °C, or by recrystallization from acetone. This compound is obtained in 88 % yield as dark blue crystals of m.p. 163 °C (decomp.). Its UV spectrum [λ_{max} = 236 mμ (log ε = 4.21), 329 (4.42), 384 (4.04), 618 (2.56) in CH_2Cl_2] resembles that of hexaphenylpentalene [1] and agrees satisfactorily with the results of an SCF–CI calculation [4]. The NMR spectrum (in [D_6]-acetone) proves the structure of (7), showing, besides the A_2B system of the unsubstituted five-membered ring [doublet centered at τ = 4.31 (H-4, H-6), triplet centered at τ = 4.66 (H-5, J_{AB} = 3.4 Hz)], a singlet for the protons of two equivalent dimethylamino groups at τ = 6.92, as well as a singlet shifted to high field (τ = 7.20) for the proton on C-2 (β-position of the quasidouble enamine system).

Compound (7) is stable towards atmospheric oxygen for several hours at 20 °C and dissolves in polar aprotic solvents to give deep blue solutions. It reacts with protic acids as an enamine, with protonation on C-2, regenerating (6). Catalytic hydrogenation (20 °C, 760 mm, H/Pd) leads to absorption of one mol. equivalent of H_2 and formation of (8),

(1)   (2)   (3)   (4)

(6)   (5)

(7)

44 %; yellow leaflets of m.p. 135 °C; λ_{max} = 339 mμ (log ε = 4.45) in CH_3OH; $\nu_{C=O}$ = 1650 cm^{-1} (in $CHCl_3$); NMR spectrum (in $CDCl_3$): multiplet centered at τ = 3.75 (4 ring protons), singlets at τ = 6.30 (CH_2), 6.80 [N($CH_3)_2$], and 7.05 as well as 7.15 [N($CH_3)_2$]}. A by-product is compound (4), which is separated from (3) by chromatography (neutral Al_2O_3 of activity III; eluent, ether/ethyl acetate) and forms red needles, decomposing above 140 °C (yield 2 %; λ_{max} = 219 mμ (log ε = 4.14), 285 (4.36), 399 (4.18), 455 (4.40) in CH_3OH; NMR spectrum in [D_6]dimethyl sulfoxide); multiplet centered at τ = 3.65 (7 ring protons), singlets at τ = 5.80 (CH_2) and 6.65 as well as 6.72 [N($CH_3)_2$].
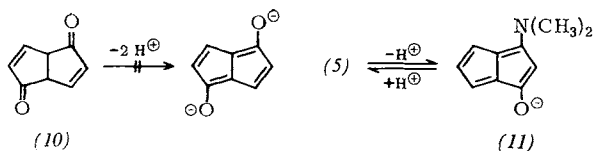
In boiling xylene (5 h) compound (3) loses dimethylamine, forming 3-(dimethylamino)-1(2H)pentalenone (5) in 63 % yield. This forms yellow needles of m.p. 225 °C and has λ_{max} = 247 mμ (log ε = 4.43), 371 (4.29) in CH_3OH, $\nu_{C=O}$ = 1675 cm^{-1} (in nujol), and an NMR spectrum (in [D_5]-pyridine) [3] with multiplets centered at τ = 3.13 (H-4, H-6) and 3.52 (H-5), and singlets at τ = 6.58 (CH_2) and 6.91 as well as 7.03 [N($CH_2)_2$]. With dimethylammonium perchlorate in CH_2Cl_2/CH_3OH (3:1 v/v), compound (5)

which is also obtained by reduction of (6) with $NaBH_4$ in H_2O and forms yellowish leaflets of m.p. 72 °C, λ_{max} = 319 mμ (log ε = 4.39) in n-hexane; its NMR spectrum (in $CDCl_3$)

(7) $\xrightarrow{H_2/Pd}$ (8) $\xrightarrow{H_2/Pd}$ (9)
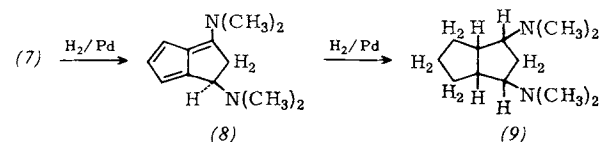
has 3 multiplets centered at τ = 3.39 (H-5), 3.89 (H-4, H-6), 5.82 (H-1), singlets at τ = 6.76 and 6.81 [N($CH_3)_2$ on C-3], a multiplet centered at τ = 6.92 (CH_2), and a singlet at τ = 7.72 [N($CH_3)_2$ on C-1]. Further hydrogenation of (8), which requires three moles of H_2, affords (9) as a colorless oil.

Whereas 1,4-pentalenedione (10) is not enolized in the presence of strong bases [5], compound (5) is readily converted by potassium t-butoxide in t-butyl alcohol into the blue enolate (11), whose UV spectrum resembles as that of (7). Hydrolysis of (11) regenerates (5).

$$\text{(10)} \xrightarrow[\text{-2 H}^{\oplus}]{} \quad (5) \quad \underset{+\text{H}^{\oplus}}{\overset{-\text{H}^{\oplus}}{\rightleftharpoons}} \quad \text{(11)}$$

(10)   *(11)*

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1,5-Cyclooctadienenickel Bromide and Iodide

By *L. Porri, G. Vitulli, and M. C. Gallazzi* [*]

We have prepared two new nickel complexes, namely, 1,5-cyclooctadienenickel bromide, $C_8H_{12}NiBr$, and iodide, $C_8H_{12}NiI$. A π-allylnickel halide is treated with 1,5-cyclo-octadiene (20- to 30-fold excess) in n-heptane in the presence of norbornene (slight excess) at room temperature. The complex separates as well-formed crystals two to three hours after the beginning of the reaction, the yield being *ca.* 75 % after 15 hours.

The complex $C_8H_{12}NiI$ can also be obtained (about 80 % yield) directly by heating a solution of π-allylnickel iodide in 1,5-cyclooctadiene to *ca.* 80 °C and then slowly cooling the mixture. The less stable bromide could not be obtained in this way.

The two cyclooctadienenickel halides are very sensitive to air. They dissolve slightly (*ca.* 1.5 wt.-%) in cyclooctadiene and these solutions are stable in absence of oxygen. Both compounds dissolve in benzene, tetrahydrofuran, or ethanol; these solutions, however, decompose rapidly, even under nitrogen, with formation of metallic nickel, nickel halide, and 1,5-cyclooctadiene, but they are stable if small amounts (2–3 %) of free cyclooctadiene are added.

There is no band at 1667 or 1486 cm⁻¹ in the IR spectrum of either compound, which indicates that both double bonds of the cyclooctadiene are coordinated to the nickel atom.

The magnetic moments of the solid complexes could not be determined because of the low stability. However, reaction with triphenylphosphine in benzene at room temperature gave the known [1] complexes $(C_6H_5P)_3NiX$, whose magnetic moments (*ca.* 1.9 B.M. for the bromide, *ca.* 1.98 B.M. for the iodide) correspond to an unpaired electron; the presence of nickel(I) in these complexes is thus indicated.

The $(C_8H_{12})NiX$ complexes react readily, even at room temperature, with benzonitrile, acrylonitrile, quinones, or esters of unsaturated carboxylic acids, with formation of new complexes in which the cyclooctadiene is replaced by another ligand. The $(C_8H_{12})NiX$ complexes catalyse polymerisation of butadiene, allene, or acetylene to linear polymers [2].

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Radical Formation on Heating of Trityl-aluminum or -boron Compounds

By *H. Hoberg* and *E. Ziegler* [*]

Trityl-aluminum and -boron derivatives are accessible from the corresponding chlorides and triphenylmethylsodium in ether [**]:

$$X_2MCl + (C_6H_5)_3CNa \rightarrow X_2M–C(C_6H_5)_3 + NaCl$$
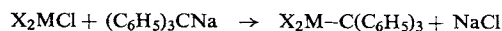
$$M = Al \text{ or } B; \; X = Cl, \text{ alkyl, or phenyl}$$

Diphenyltritylaluminum, $(C_6H_5)_2Al–C(C_6H_5)_3$, m.p. 205 °C (decomp.), can also be obtained by the action of diphenyldiazomethane on triphenylaluminum in anisole at 20 °C:

$$(C_6H_5)_2CN_2 + (C_6H_5)_3Al \rightarrow (C_6H_5)_2Al–C(C_6H_5)_3 + N_2$$

Like the central C–C bond of hexaphenylethane, the $M–C_{(trityl)}$ bond of trityl-aluminum and -boron compounds readily undergoes homolysis. For colorless diphenyltrityl-aluminum, this homolysis, which occurs at 130 °C in the solid state, is demonstrated by an intense yellow coloration and by development of the ESR signal of triphenylmethyl. Also, on pyrolysis in an aliphatic or aromatic hydrocarbon, aluminum separates after several hours' heating at 130 °C; deposition of aluminum is observed only above 240 °C for trialkylaluminums [1].

$$3 \; X_2Al–C(C_6H_5)_3 \rightarrow [3 \; X_2Al\bullet] + (C_6H_5)_3C\bullet$$
$$\downarrow$$
$$2 \; AlX_3 + Al$$
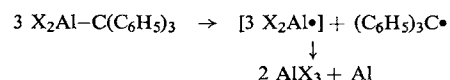
The aluminum radical can be trapped by a primary or secondary amine, the separation of aluminum being thus prevented.

$$R_2Al–C(C_6H_5)_3 + R_2'NH \rightarrow R_2Al–NR_2' + (C_6H_5)_3CH$$
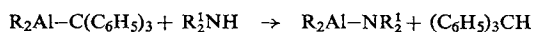
If pyrolysis is effected in the presence of pyridine bases [2], colored solutions containing radicals with Al–N bonds are formed whose ESR spectra (20 °C) are no longer identical with that of triphenylmethyl [the trityl radical reacts with the solvent at the reaction temperature (130 °C), yielding $(C_6H_5)_3CH$]. The hyperfine structure of these spectra is so little developed that the number and type of the nuclei (H, N, Al) concerned in the splitting cannot be determined. On pyrolysis of tritylaluminum dichloride in pyridine a deep blue solution is obtained whose ESR spectrum shows a hyperfine structure of 57 lines; the same spectrum develops on dehalogenation of $AlCl_3$ with sodium or on cathodic reduction in pyridine [3].

Pyrolysis of dialkyltritylboron in quinoline or isoquinoline also affords colored solutions containing radicals with B–N bonds. The ESR spectra show resolution into 10 equidistant HFS lines, with a relative separation of 4.10 or 4.17 gauss, that is interpreted as due to coupling of the electrons with

452

Angew. Chem. internat. Edit. / *Vol. 6 (1967)* / *No. 5*