[4] Cf. [2]; it has not yet been possible to decide experimentally whether in the cyclization in boiling piperidine we are dealing with an electrocyclic reaction or with an intramolecular electrophilic substitution of the five-membered ring after attack by the base at position 6 of the fulvenoid system.

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[9] R. B. Woodward and R. Hoffmann, Angew. Chem. 81, 797 (1969); Angew. Chem. internat. Edit. 8, 781 (1969); cf. J. J. Gajewski and C. J. Cavender, Tetrahedron Lett. 1971, 1057.

Concerning Pentalene, 2-Methylpentalene, and 1,3-Dimethylpentalene[**]

By Klaus Hafner, Reinhard Dönges, Ernst Goedecke, and Reinhard Kaiser[*]

In the series of non-alternant bicyclic hydrocarbons, pentalene (1) has, unlike azulene (2)[1] and heptalene (3)[2],

(1)   (2)   (3)
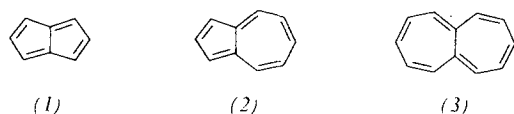
withstood attempts at synthesis that have extended over decades[3]. Each of the three compounds contains a peripheral π-electron system perturbed by a central σ-bond;

(6)

(7)   (4)

(8)

(9)
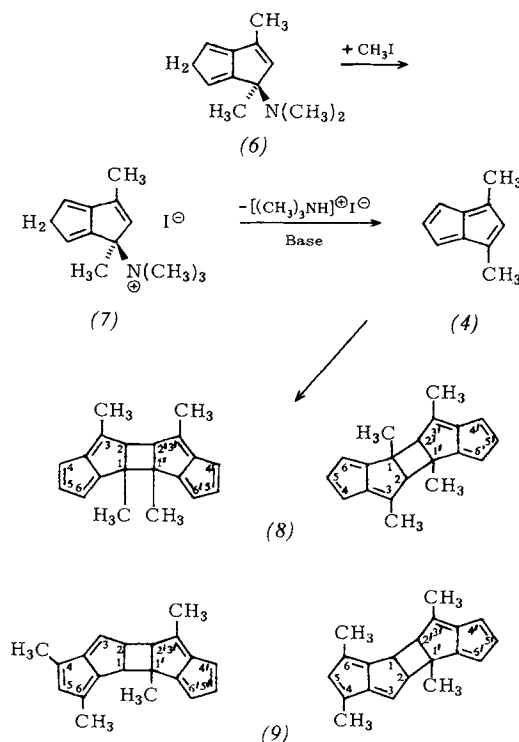
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in the case of azulene (2), isomeric with naphthalene and having 10 π-electrons, the system has "aromatic" character, whereas heptalene (3) with 12 π-electrons behaves as a cyclopolyolefin. According to the Hückel rule, pentalene, with 8 π-electrons, should not have "aromatic" properties, but quantum-chemical calculations have given contradictory results[4]. Since it is not permissible to draw conclusions about the parent compound from the few known benzo-annelated or highly substituted pentalene derivatives, it is of interest to test the theoretical predictions by synthesis of (1) or its simple alkyl derivatives.

Starting from 1,2- and 1,5-dihydropentalene derivatives, for which we have described a simple method of preparation[5–7], we have now been able to detect pentalene (1),

Table 1. Physical properties of the products (8), (9), (12), and (14).

Cpd.	Yield (%)	M.p. [°C]	UV λ_{max} (nm) (log ε) in n-hexane	NMR (τ), J (Hz) in CCl_4 [a]
(8a)	32	110–112	267 (4.38) 379 (3.14)	8.43 (CH_3-1/s), 6.91 (H-2/m), 8.00 (CH_3-3/s), 4.16 (H-4/dd), 3.45 (H-5/dd), 4.31 (H-6/m), $J_{4,5}=5.5$, $J_{4,6}=0.5$, $J_{5,6}=2$
(8b)	1.6	80 (dec.)	261, 389	8.65 (CH_3-1/s), 6.53 (H-2/m), 7.95 (CH_3-3/s), 4.26 (H-4/dd), 3.50 (H-5/m), 4.59 (H-6/m), $J_{4,5}=5.5$, $J_{4,6}=0.5$, $J_{5,6}=2$
(8c)	4	180 (dec.)	259 (4.31) 267 (4.38) 284 (4.08) 404 (3.23)	9.03 (CH_3-1/s), 7.30 (H-2/m), 7.81 (CH_3-3/s), 3.98 (H-4/dd), 3.30 (H-5/dd), 4.20 (H-6/m), $J_{4,5}=5$, $J_{4,6}=0.5$, $J_{5,6}=2$
(9a)	4,5	150 (dec.)	256 (4.22) 262 (4.24) 279 (4.05) 408 (3.21)	7.17 (m), 6.61 (m), 6.92 (m) (H-1, H-2, H-2'), 9.05 (CH_3-1'/s), 3.58 (H-3/d), 7.83 (CH_3-3'/s), 7.99 (CH_3-4/d), 4.00 (H-4'/dd), 3.80 (H-5/m), 3.32 (H-5'/dd), 8.10 (CH_3-6/s), 4.25 (H-6'/m), $J_{2,3}=3$, $J_{4,5}=0.5$, $J_{4',5'}=5$, $J_{4',6'}=0.5$, $J_{5',6'}=2$
(9b)	6			6.80 (m), 6.67 (m), 6.50 (m) (H-1, H-2, H-2'), 8.52 (CH_3-1'/s), 3.95–4.00 (H-3, H-5/m), 7.99 (CH_3-3'/s), 8.13 (CH_3-4/d), 4.16 (H-4'/dd), 3.48 (H-5'/dd), 8.23 (CH_3-6/s), 4.49 (H-6'/d), $J_{4',5'}=5$, $J_{4',6'}=1$, $J_{5',6'}=2$
(12a)	22	103–104 (dec.)	254 (4.16) 387 (3.02)	6.25–6.43 (H-1/dm), 5.69–5.99 (H-2/dm), 3.71 (H-3/m), 4.11 (H-4/dd), 3.33 (H-5/dd), 4.35 (H-6/m), $J_{4,5}=5$, $J_{4,6}=0.8$, $J_{5,6}=1.8$
(12b)	10	84 (dec.)	254 (4.21) 259 (4.22) 275 (4.07) 400 (3.17)	7.05 (H-1/dm), 6.39 (H-2/dm), 3.26 (H-3/m), 3.92 (H-4/dd), 3.23 (H-5/dd), 4.01 (H-6/m), $J_{4,5}=5.1$, $J_{4,6}=0.7$, $J_{5,6}=1.8$
(14a)	26	106–107 (dec.)	257 (4.20) 272 (4.11) 382 (2.90)	6.35–6.53 (H-1/m), 5.84–6.04 (H-2/m), 3.97 (H-3/m), 4.43 (H-4/m), 8.00 (CH_3-5/s), 4.52 (H-6/m)
(14b)	12	140 (dec.)	258 (4.25) 263 (4.28) 276 (4.15) 392 (3.06)	7.00–7.13 (H-1/m), 6.38–6.56 (H-2/m), 3.48 (H-3/m), 4.22 (H-4/m), 7.88 (CH_3-5/s), 4.15 (H-6/m)

[a] TMS as internal standard.

1,3-dimethylpentalene *(4)*, and 2-methylpentalene *(5)* directly or by formation of their dimerization products.

Treating 1-(dimethylamino)-1,5-dihydro-1,3-dimethylpentalene *(6)*[6, 7] with methyl iodide in ether at −25 °C affords the methiodide *(7)* (yield 92%, dec. >75 °C). At 25 °C *(7)* undergoes 1,4-elimination in ethanol in the presence of a base yielding 1,3-dimethylpentalene *(4)*[8], whose existence as a short-lived intermediate is strongly suggested by isolation of dimerization products of structures *(8)* and *(9)* that are formed rapidly under the experimental conditions[6]. For each of *(8)* and *(9)* four configurations around the cyclobutane ring are possible and, of these, three stereoisomers were isolated for *(8)* [*(8a)*, *(8b)*, and *(8c)*] and two for *(9)* [*(9a)* and *(9b)*] (see Table 1).

On photolysis[9] of the dimer *(8a)* in a methylcyclohexane/2-methylbutane matrix (1:4) at −196 °C by means of monochromatic light of wavelength 254 nm, the extinctions of the maxima of *(8a)* were observed to decrease whilst a new maximum was formed at 336 nm (Figure 1).
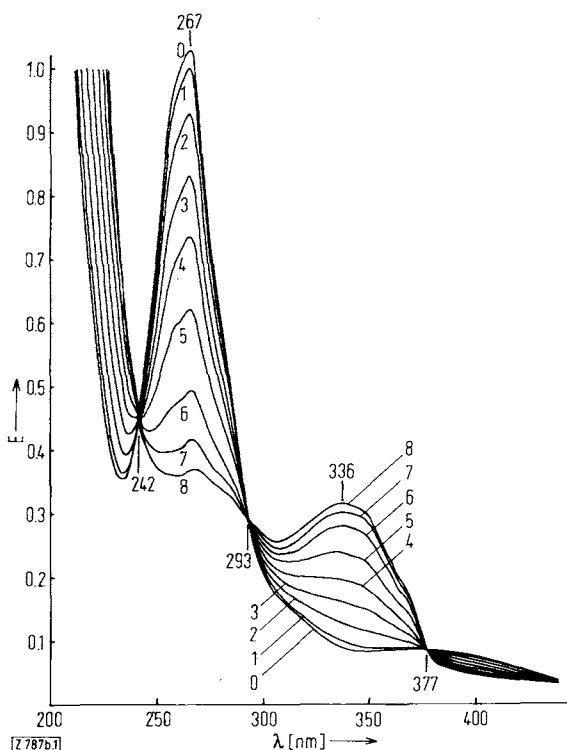

Fig. 1. Photolysis of the dimer *(8a)* (curve 0) to yield 1,3-dimethylpentalene *(4)* (curve 8). The absorption curves 1 to 8 were measured after 15 min. 1, 2, 4, 6, 10, and 25 h, respectively.

When the matrix was warmed to 20 °C this photochemical rearrangement, characterized by three isosbestic points, was seen to be thermally largely reversible. The absorptions of the product from *(8a)* are in excellent agreement with the values determined quantum-chemically for absorption by *(1)*[4d] and accord with the data of *de Mayo et al.* for 1-methylpentalene[10]. Thus the photochemical conversion of the dimeric 1,3-dimethylpentalene *(8a)* may be a [2+2]-cycloreversion with formation of 1,3-dimethylpentalene *(4)*.

For preparation of pentalene *(1)* 1,2-dihydro-1-piperidino-pentalene *(10)*[11] [a yellow thermolabile oil; λmax (logε)=257 (3.98), 260 (3.97), 264 (3.94), 275 (3.65), 340 nm (3.08) in n-hexane; NMR spectrum (in CCl₄): multiplets
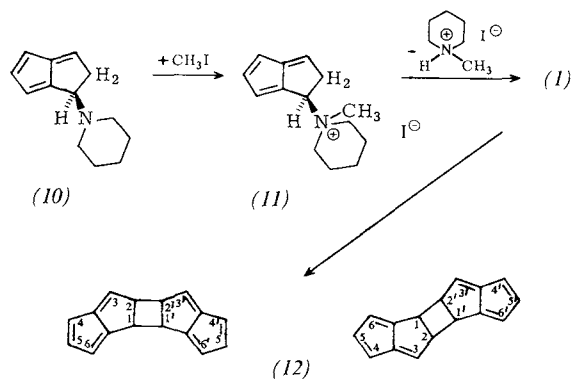
centered at τ=3.28 (H-5), 3.44 (H-3), 4.00 (H-4, H-6), 6.01 (H-1), 6.97 (2H-2), 7.62 and 8.57 (C₅H₁₀N)] was converted into the methiodide *(11)* (yield 47%, dec. >100 °C) by methyl iodide in ether at −25 °C. In ethanol in the presence of a base this underwent Hofmann degradation at a temperature as low as 20 °C, after which two pentalene dimers of structures *(12)* were isolated in 22 and 10% yield, respectively; they are stereoisomers of *(12)* with respect to the cyclobutane ring fusions[12] (see Table 1).

The results of photolysis of the dimers *(12a)* and *(12b)* under the same conditions as for the dimer *(8a)* indicate a fission of the dimers here too.

Analogously to the formation of the dimers of 1,3-dimethylpentalene *(4)*, two dimers *(14)* (or their stereoisomers with respect to the cyclobutane ring fusions) (Table 1) of the presumed intermediate 2-methylpentalene *(5)* were isolated from 1-(dimethylamino)-1,5-dihydro-2-methylpentalene *(13)*[7].
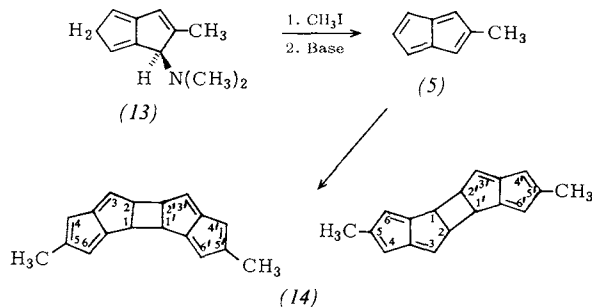
Experiments are at present being carried out in an attempt to identify the pentalene *(1)* and its derivatives *(4)* and *(5)*.

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[7] *R. Kaiser* and *K. Hafner,* Angew. Chem. 85, 361 (1973); Angew. Chem. internat. Edit. 12, 335 (1973).

[8] On thermolysis 1-(dimethylamino)-1,2-dihydro-1,3-dimethylpentalene [isomeric with *(6)*] [7] or its methiodide or N-oxide affords 1,2-dihydro-3-methyl-1-methylenepentalene as a red oil, sensitive to oxygen

338

Angew. Chem. internat. Edit. / Vol. 12 (1973) / No. 4

$[\lambda_{max}$ (log ε) = 214 (4.16), 221.5 (4.00), 237.5 (4.06), 244.5 (4.18), 253 (4.18), 263 (3.95), 273 (4.00), 285 (3.91), 406 nm (3.22) in n-hexane; NMR spectrum (CDCl$_3$): τ = 4.87, 4.43 (m, 2H-9), 6.33 (m, 2H-2), 7.70 (m, CH$_3$-3), 3.45—3.62 (m, H-4, H-6), 2.82—3.03 (m, H-5)].

[9] We thank Prof. G. Quinkert, Dipl.-Chem. K. Kaiser, and Dipl.-Chem. K. Schmieder (Universität Frankfurt/Main) for advice and help in carrying out the photolyses.

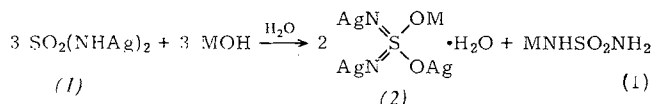[10] R. Bloch, R. A. Marty, and P. deMayo, J. Amer. Chem. Soc. 93, 3071 (1971); Bull. Soc. Chim. France, 1972, 2031.

[11] Reduction of 1,2-dihydro-1,3-dipiperidinopentalene (pale yellow crystals, m. p. 99 C) by lithium tetrahydridoaluminate gave (10) in 65% yield. The starting material can be prepared by condensation of sodium cyclopentadienide with 3-(dimethylamino)-3-ethoxy-N,N-dimethyl-propen-2-aldiminium tetrafluoroborate, which gives 6-(2'-ethoxy-2'-dimethylaminovinyl)fulvene (red needles, m. p. 54 C, yield 70%), with final cyclization in boiling piperidine (yield 46%).

[12] Primary formation of pentalene (1) before formation of the dimers is also indicated by isolation of the dimer (12a) on dehydrogenation of 1,2-dihydropentalene [5] at 480°C in presence of a Pd/C catalyst in vacuo.

Dinitridodioxosulfate(VI), SN$_2$O$_2^{4-}$: A New Derivative of the Sulfate Ion
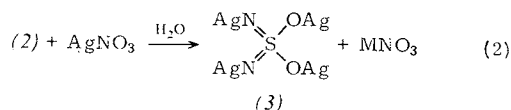
By Edgar Nachbaur and Alois Popitsch[*]

Reaction of sulfuric diamide with silver nitrate in aqueous solution followed by neutralization with ammonia gives the sparingly soluble, white N,N'-diargentosulfuric diamide (1)[1]. This is converted by alkali hydroxide or ammonia solution in excess into yellow products with a higher silver content. For example, (1) and 2 N NaOH at room temperature give monosodium trisilver dinitridodioxosulfate(VI) monohydrate (2) (M = Na) and N-sodiosulfuric diamide; the former is also only sparingly soluble, but the latter remains in solution.

$$3\ SO_2(NHAg)_2 + 3\ MOH \xrightarrow{H_2O} 2\ \begin{array}{c} AgN \searrow \nearrow OM \\ S \\ AgN \nearrow \searrow OAg \end{array} \cdot H_2O + MNHSO_2NH_2 \quad (1)$$

(1)   (2)

M = Li, Na, K, NH$_4$

Reaction of (2) with hydrogen sulfide in anhydrous methanol affords a mixture of sulfuric diamide and sodiosulfuric diamide, as can be demonstrated spectroscopically, and this confirms the stoichiometry of eq. (1).

On digestion of (2) with an excess of warm aqueous silver nitrate solution one obtains the insoluble dark red tetrasilver dinitridodioxosulfate(VI) (3):

$$(2) + AgNO_3 \xrightarrow{H_2O} \begin{array}{c} AgN \searrow \nearrow OAg \\ S \\ AgN \nearrow \searrow OAg \end{array} + MNO_3 \quad (2)$$

(3)

If (3) is treated in the same way with H$_2$S, then sulfuric diamide is quantitatively regenerated. The composition of (2) and (3) is proved by elemental analysis. The IR spectra accord with the tetrahedral structure (C$_{2v}$) assumed for the SN$_2$O$_2^{4-}$ ion: IR spectrum of (3) (KBr; cm^{-1}): 1080 v_{as}(S=N) vs; 935 v_s(S=N) vs; 890 v_{as}(S—O) vs; 785 v_s(S—O) vs; 670 s, 620 s, 580 s, 375 s.

The silver salts (2) and (3) are insoluble in all the usual solvents and are thermally unstable, particularly com-

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pound (3) which in the dry state decomposes explosively on mechanical shock (rubbing, impact) with deposition of metallic Ag.

Experimental:

Concentrated NH$_3$ solution (100 ml) is added to SO$_2$(NH$_2$)$_2$ (4.8 g, 0.05 mol) and AgNO$_3$ (17 g, 0.1 mol) under red light, and the mixture is concentrated to 10 ml in a rotary evaporator. The white crystalline precipitate (1) is filtered off and washed with water; when heated with 5% NH$_3$ solution in excess it changes almost quantitatively to the pale yellow trisilver salt (2).

The salt (2) (1 g) is digested with AgNO$_3$ (5 g) in H$_2$O (100 ml) in a beaker protected from light and heated on a water-bath. Dark red tetrasilver salt (3) is then formed and can be washed with water, alcohol, and ether and stored under an inert solvent. Yield almost 100%.

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^{13}C^{13}C Coupling Constants of 1,3-Butadiene[**]

By Georg Becher, Wolfgang Lüttke, and Gerd Schrumpf[*]

The bonding in 1,3-butadiene is of fundamental importance in the question of the extent of delocalization of the π-electrons of unsaturated molecules. Increased interest attaches to ^{13}C^{13}C coupling constants for the study of CC bonding[1]. There exists a direct relation[2], which also has a theoretical foundation[3], between the extent of this coupling and the properties of the C atoms participating in the bonding. Thus, we have determined the ^{13}C^{13}C coupling constants of 1,3-butadiene[4]. Since it is not possible, even with the techniques available today, to measure these constants precisely for compounds with their natural ^{13}C content, we have analyzed the spectra of several ^{13}C-labeled butadiene molecules. Butadienes were therefore prepared containing one or two ^{13}C atoms enriched to ca. 90%.

The coupling constant between non-equivalent ^{13}C atoms can be determined on introduction of only one ^{13}C atom by measuring its coupling with the other ^{13}C atoms left in their natural abundance. The coupling constants are obtained from such ^{13}C-NMR spectra by simultaneous decoupling of all the protons.

It becomes necessary to introduce two ^{13}C atoms when the coupling constant between chemically equivalent ^{13}C nuclei is to be measured. The coupling constant can be determined from the spectrum only if the two ^{13}C nuclei couple with other nuclei, e. g. with protons. For such spin systems all the coupling constants can be found from both the ^{13}C- and the ^{1}H-NMR spectrum[5].

To avoid too complicated spectra, as few protons as possible were left in the ^{13}C-labeled molecule; the unnecessary hydrogen atoms were replaced by deuterium, and the spectra were observed under D-decoupling conditions.

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