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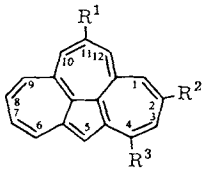
Azuleno[8,8a,1,2-*def*]heptalene

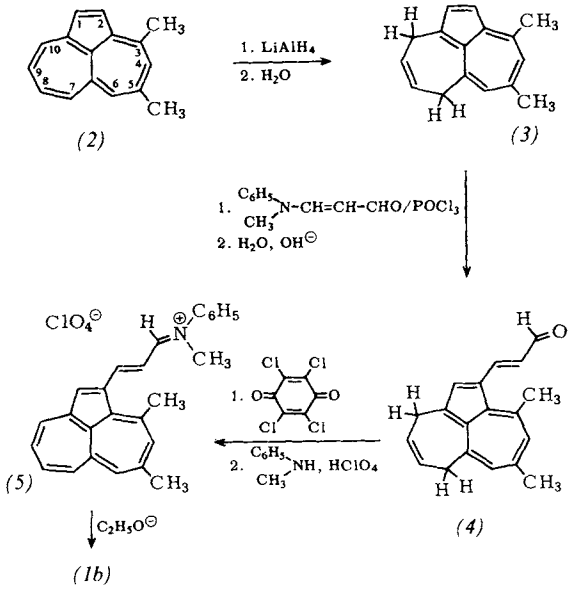
By *K. Hafner, G. Hafner-Schneider,* and *F. Bauer* [*]

Methyl derivatives of the still unknown hydrocarbon *(1a)* azuleno[8,8a,1,2-*def*]heptalene (dicyclohept[*cd-ij*]azulene) can be prepared by a simple process that has already repeatedly proved its value for preparation of polycyclic condensed



(1a), $R^1 = R^2 = R^3 = H$
(1b), $R^1 = CH_3$, $R^2 = R^3 = H$
(1c), $R^1 = R^2 = R^3 = CH_3$

non-benzenoid systems [1]. 11-Methylazuleno[8,8a,1,2-*def*]-heptalene *(1b)* is accessible from 3,5-dimethylaceheptylene *(2)* [2] by base-catalyzed intramolecular cyclization of the aldimmonium perchlorate *(5)*. The salt *(5)* cannot be prepared from *(2)* by the Vilsmeier reaction with 3-(*N*-methylanilino)acrolein and $POCl_3$ [3], since *(2)* is preferentially substituted in the 1- and 4- or 9-, and 6- or 7-positions by electrophiles. It can, however, be obtained by way of 7,10-dihydro-3,5-dimethylaceheptylene *(3)*, which is formed in 65–70% yield on partial reduction of *(2)* by $LiAlH_4$ in boiling tetrahydrofuran [dark blue crystals of m.p. 74–76 °C (from light petroleum) [4]].



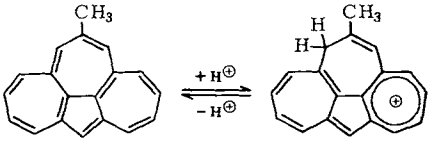
(2) *(3)* *(5)* *(4)* *(1b)*

As a derivative of azulene, compound *(3)* is substituted exclusively at C-2 by electrophilic reagents. On reaction with 3-(*N*-methylanilino)acrolein and $POCl_3$ in tetrahydrofuran and subsequent alkaline hydrolysis, *(3)* affords the propenal *(4)* [yield, 81%; dark green needles of m.p. 150 to 151 °C (from ethyl acetate) [5]], dehydrogenation of which by chloranil in boiling benzene gives 3-(3,5-dimethyl-2-aceheptylenyl)acrolein [yield, 68%; reddish-brown needles of m.p. 109–110 °C (from ethyl acetate) [5]]. Treatment with *N*-methylaniline and 70% perchloric acid in tetrahydrofuran leads to a 98% yield of the aldimmonium perchlorate *(5)* (black crystals, decomp. > 230 °C), which in the presence of sodium ethoxide in boiling ethanol condense to the thermally stable hydrocarbon *(1b)* [yield 7%; dark green needles of m.p. 115–116 °C (from light petroleum); trinitrobenzene adduct, black needles of m.p. 182–184 °C (from ethanol)].

Elemental analysis, molecular-weight determination, and UV and NMR spectra prove the constitution of *(1b)*.

The banded electronic spectrum of *(1b)* in *n*-hexane shows absorption maxima at 233 nm (log ε = 4.40), 276 (4.53), 299 (4.88), 337 (3.88), 398 (3.67), 507 (sh) (2.44), 539 (2.27), 583 (2.24), 638 (2.10), 930 (1.64), 1075 (1.74), 1275 (1.72), and 1630 (1.40). The unusually long-wave absorption of this 18 π-electron system accords satisfactorily with the result of an SCF calculation [6]. In the NMR spectrum of *(1b)* in CS_2 the proton signals are at notably high field: as well as the singlet of the five-ring proton H^5 at $\tau = 5.42$, there is the ABCD spectrum of the eight protons of the two unsubstituted seven-rings (H^1–H^4, H^6–H^9) at $\tau = 5.46$, 6.31, 6.04, and 7.12; a broadened singlet at $\tau = 8.02$ is to be ascribed to the two equivalent protons H^{10} and H^{12}, and a triplet at $\tau = 9.68$ (allylic coupling with H^{10} and H^{12}; $J = 0.6$ Hz) to the methyl protons. The positions of the signals indicate a strong paramagnetic ring current in the three seven-membered rings and a weak diamagnetic ring current in the five-membered ring [7].

Compound *(1b)* is strongly basic. The reversible protonation, occurring even in 2N H_2SO_4, leads to the reddish-violet conjugated acid *(6)* [UV spectrum of *(1b)* in CH_2Cl_2/



(1b) *(6)*

CF_3COOH: $\lambda_{max} = 326$ nm (log ε = 4.71) 402 (3.92), 423 (3.91), 551 (4.05), 645 (3.05), and 715 (2.52)], which is formally a combination of the azulene with the heptalenium cation [8]. The NMR spectrum of *(6)* [H^1–H^9, 2 multiplets centered at $\tau = 1.62$ (7H) and $\tau = 0.90$ (2H); H^{12}, broad singlet at $\tau = 2.66$; CH_2 (in position 10), singlet at $\tau = 6.12$; CH_3, doublet at $\tau = 7.32$ (allylic coupling with H^{12}, $J = 1.2$ Hz] confirms the protonation at position 10 (≡ 12), as does the SCF calculation [6] for *(1b)* according to which these positions have the highest electron density.

2,4,11-Trimethylazuleno[8,8a,1,2-*def*]heptalene *(1c)* can be prepared analogously to *(1b)* from 3,5,8,10-tetramethylaceheptylene [9] [yield, 7%; dark green cuboids of m.p. 106 to 107 °C (from light petroleum); trinitrobenzene adduct, black needles, decomp. > 190 °C (from ethanol)] by intramolecular cyclization of the aldimmonium perchlorate corresponding to *(5)* (yield, 97%, bluish-black crystals of m.p. 200 to 202 °C). This product *(1c)* has the same chemical and physical properties as hydrocarbon *(1b)*.

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[4] *K. Hafner* and *G. Schneider*, Liebigs Ann. Chem. *672*, 194 (1964); on reduction of *(2)* by $LiAlH_4$ the main product *(3)* was accompanied by small amounts of the 7,8- and 9,10-dihydro derivatives.

[5] All the substances described gave correct analytical results.

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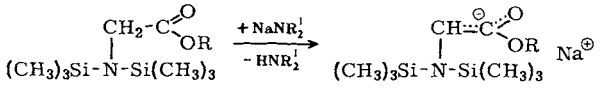
[9] *K. Hafner* and *G. Hafner-Schneider*, unpublished work; 4,6,8-trimethylazulene and 4-diethylamino-3-penten-2-one afforded 3,5,8,10-tetramethylaceheptylene in a synthesis analogous to that of *(2)* [2]. This aceheptylene derivative reacts preferentially with substitution in positions 4 and 6 on treatment with 3-*N*-methylanilinoacrolein/$POCl_3$; 3-(3,5,8,10-tetramethylaceheptylen-1-yl)acrolein is formed only as a by-product (25%).

Synthesis of Amino Acids from *N,N*-Bis(trimethylsilyl)glycine Esters [1]

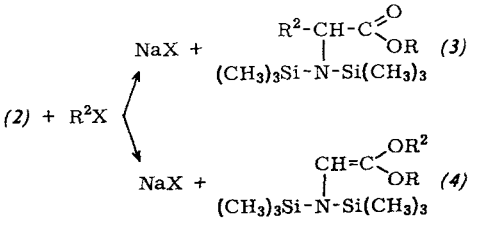
By *K. Rühlmann* and *G. Kuhrt* [*]

During our work on *N,N*-bis(trimethylsilyl)amines [2] we have found a very convenient and general synthesis of amino acids. *N,N*-Bis(trimethylsilyl)glycine esters *(1)* are first converted into the sodio derivatives *(2)* (not isolated) by means of Na bis(trimethylsilyl)amide or another base. The compounds *(2)* can undergo nucleophilic substitution or addition. The



(1a), R = C_2H_5 R^1 = H, $Si(CH_3)_3$ *(2a)*, R = C_2H_5
(1b), R = $Si(CH_3)_3$ *(2b)*, R = $Si(CH_3)_3$

C-substitution products *(3)* are obtained on reaction with alkyl halides, and *O*-substitution products *(4)* on reaction with trimethylsilyl chloride (see Table 1).

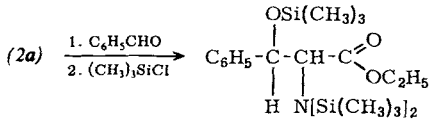


All the Si–O and Si–N bonds in compounds *(3)* and *(4)* are rapidly and completely cleaved by dilute aqueous or ethereal HCl. Thus ethyl amino-ester hydrochlorides are obtained from *(3a)–(3d)*, glycine ethyl ester hydrochloride from *(4a)*, and glycine from *(4b)*.

Table 1. Ethyl *N,N*-bis(trimethylsilyl)amino esters *(3)* and *N,N*-bis(trimethylsilyl)aminoketene acetals *(4)*.

Cpd.	R	R^2	X	B.p. (°C/torr)	n_D^{20}	Yield (%)
(3a)	C_2H_5	CH_3	I	110/111	1.4422	55
(3b)	C_2H_5	C_2H_5	I	115–117/12	1.4460	65
(3c)	C_2H_5	C_6H_5–CH_2	Br	179–181/10	1.4952	70
(3d)	C_2H_5	$(CH_3)_2HSi$–CH_2	I	133–134/10	1.4518	52
(4a)	C_2H_5	$(CH_3)_3Si$	Cl	118/9	1.4430	77
(4b)	$(CH_3)_3Si$	$(CH_3)_3Si$	Cl	122–126/10	1.4397	67

On treatment with aldehydes, *(1a)* loses hexamethyldisiloxane to afford imines, and *(2a)* gives salts of ethyl α-amino esters which can be converted into *N,N,O*-tris(trimethylsilyl) derivatives by trimethylsilyl chloride. As an example we



(5)

report the reaction with benzaldehyde yielding 3-phenyl-*N,N,O*-tris(trimethylsilyl)serine ethyl ester *(5)*, b.p. 115 °C/0.5 torr, n_D^{20} = 1.4703. This product, which is accessible in good yield, is hydrolyzed by dilute HCl to phenylserine ethyl ester hydrochloride, m.p. 170 °C [3].

N,N-Bis(trimethylsilyl)glycine ester (1):
Glycine ethyl ester or glycine is heated with an excess of (trimethylsilyl)diethylamine in the presence of a catalytic amount of $(NH_4)_2SO_4$ at *ca.* 120 °C until no more diethylamine distils off. For purification the residue is distilled in a vacuum. *(1a)*, b.p. 100 °C/10 torr, n_D^{20} = 1.4369, is formed in 75 % yield from glycine ethyl ester, and *(1b)*, b.p. 106–108 °C/10 torr, n_D^{20} = 1.4341, in 90 % yield from glycine.

Ethyl N,N-bis(trimethylsilyl)amino esters (3):
0.055 mole of Na bis(trimethylsilyl)amide in 100 ml of ether is added to 0.05 mole of *(1a)* in 50 ml of ether at −10 ° to 0 °C with stirring and the mixture is kept at room temperature for a short time. 0.05 mole of R^2X is then added dropwise and the whole is heated at the b.p. for 10–15 h, then filtered and distilled. *(4a)* is formed under analogous conditions; the synthesis of *(4b)* is carried out at −60 °C.

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Quinodimethanes from 1,2-Diaryl-3-ethoxycyclopropenylium Ions

By *K. Eiglmeier* and *Th. Eicher* [*]

1,2-Diaryl-3-ethoxycyclopropenylium salts *(1)* [1] (X = BF_4) react with arylmalononitriles *(2)* in the presence of a base, preferably *N*-ethyldiisopropylamine (Hünig base), with formation of 1:1-adducts *(3)*.

The 3-ethoxy-1-cyclopropene structure of the adducts follows unambiguously from the IR spectra (cyclopropene bands [2] at *ca.* 1800 cm^{-1}) and the NMR spectra [CH_2 quadruplet of an