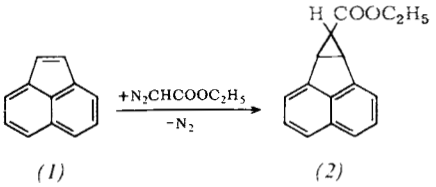
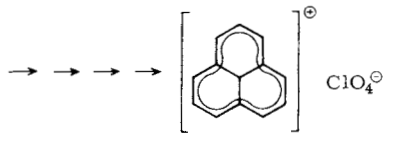
New Synthesis of 2*H*-Benzazulenes

By *Klaus Hafner* and *Wolfgang Rieper* [*]

Acenaphthylene *(1)* combines with ethoxycarbonylcarbene, generated by thermolysis of ethyl diazoacetate, to give the stable cyclopropane derivative *(2)*, which can be converted into phenalenium perchlorate *(3)* *via* a multi-step synthesis [1].



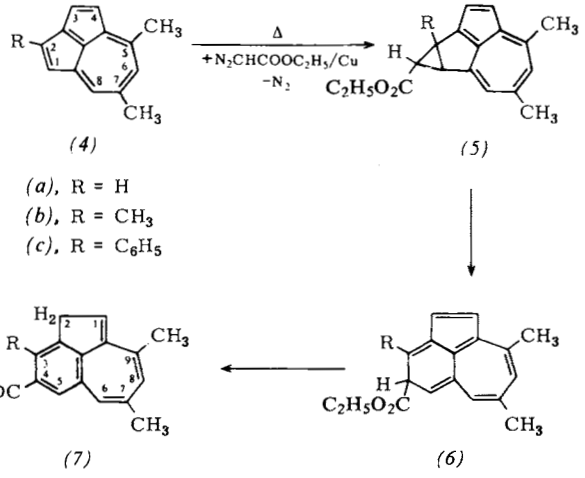
(1) *(2)*



(3)

The derivatives *(4a)*—*(4c)* of cyclopent[*cd*]azulene, an isomer of *(1)*, react similarly with carbenes (carbenoids) to yield 1,2-cycloaddition products. Unlike *(2)*, however, these products isomerize under the reaction conditions to the hitherto rather inaccessible 2*H*-benz[*cd*]azulene system *(7)* [2] which warrants interest as an isomer of phenalene.

The copper-catalyzed decomposition of ethyl diazoacetate in the presence of *(4a)* [3] in methyl cyclohexane at 90—100 °C leads directly to ethyl 7,9-dimethyl-2*H*-benz[*cd*]azulene-4-carboxylate *(7a)* (m.p. 93—94 °C) in 55—60% yield. Cycloaddition to the 1,2 bond of *(4a)* giving *(5a)* is probably followed by valence isomerization of the latter to the cross-conjugated tricyclic compound *(6a)*, which undergoes a hydrogen shift to give the stable molecules *(7a)*.



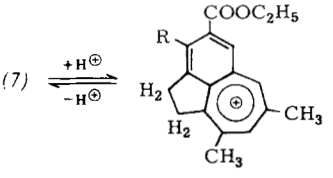
(4) *(5)*

(a), R = H
(b), R = CH_3
(c), R = C_6H_5

(7) *(6)*

Cycloaddition to the 3,4-bond of *(4a)*, which is also characterized by a high bond order, was not observed. In the case of *(4b)* and also *(4c)* [4], cycloaddition occurs exclusively at the 1,2-bond to give *(7b)* (m.p. 79—81 °C, 64%) and *(7c)* (m.p. 106—108 °C, 59%) (cf. ref. [5]).

In contrast to 2*H*-benz[*cd*]azulene [2b] and its 7,9-dimethyl derivative [6], compounds *(7a)*, *(7b)*, and *(7c)* can be isolated at room temperature and can be stored below 0 °C in the absence of atmospheric oxygen. Like 3,4,7,9-tetramethyl-2*H*-benz[*cd*]azulene [2a] they form trinitrobenzene adducts, and the heptafulvene system is reversibly protonated in position 1 to the bridged benzotropylium cation *(8)* by 70% perchloric acid. The structures of compounds *(7)* were established by elemental analysis, molecular-weight determination, and UV and NMR spectra.



(7) *(8)*

Received: December 23, 1969 [Z 143b IE]
German version: Angew. Chem. *82*, 218 (1970)

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[6] *W. Rieper*, Dissertation, Technische Hochschule Darmstadt 1968. 7,9-Dimethyl-2*H*-benz[*cd*]azulene was prepared by thermolysis of 4-(3,3-diethoxypropyl)-6,8-dimethylazulene at 150—180 °C/10^{-5} torr and isolated as the trinitrobenzene adduct [m.p. 170—171 °C (decomp.)].

CONFERENCE REPORTS

Biochemical and Genetic Aspects of Ribosome Specificity in Protein Synthesis

By *Orio Ciferri* [*]

70 S type of ribosomes, prepared from prokaryotic organisms or cell organelles (mitochondria and chloroplasts) of eukaryotic organisms, catalyze the reactions for protein synthesis *in vitro* only in the presence of polymerizing enzymes obtained from prokaryotes or organelles. No activity is evident when such ribosomes are tested in the presence of preparations of polymerizing enzymes extracted from the cytoplasm of the eukaryotic organisms. Ribosomes of the 80 S type, like those present in the cytoplasm of eukaryotes, are active *in vitro* only in the presence of preparations of polymerizing enzymes from the cytoplasm of such organisms.

Transfer factors T and G, which may be separated from the preparations of polymerizing enzymes, appear to be strictly ribosome specific. Indeed only one transfer factor T and one transfer factor G, specific for 70 S ribosomes, are present in the extract from cells of *E. coli*. In contrast, two transfer factors G and two transfer factors T, each specific for just one type of ribosome, may be detected in the non-photosynthetic eukaryotic alga *Prototheca zopfii*. Two ribosome specific transfer factors G have been demonstrated also in the case of the yeast *Saccharomyces cerevisiae*.

Extracts prepared from dark-grown cells of the photosynthetic flagellate *Euglena gracilis* display polymerizing activity only