

borane and tetraethyl diboroxide) up to 42°C/14 torr, a yellow liquid (83 g) of b. p. 71—80°C/0.08 torr is obtained. Methanol (50 ml) is added and all volatile components (bath temperature up to 100°C, pressure down to 14 torr) are distilled off to yield 74 g (85%) of a pale yellow equimolar mixture of (3a) and (3b) (GC, ¹H-NMR spectrum) of b. p. 73—74°C/0.09 torr.

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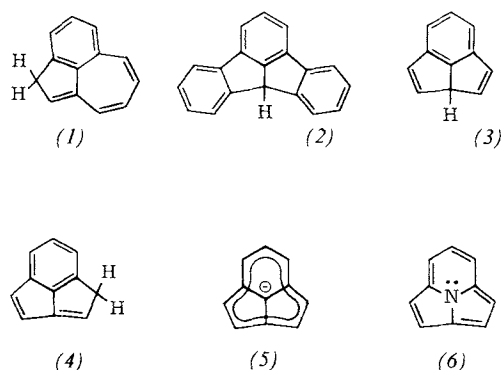
Synthesis of 1H-Cyclopent[cd]indene and its Anion^[**]

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Dedicated to Professor Walter Franke on the occasion of his 65th birthday

In connection with studies of 2H-benz[cd]azulene (1)^[1] and the strongly acidic fluoradene (2)^[2] particular interest^[2-6] attaches to the parent system of the latter, 2aH-cyclopent[cd]indene (3) and its 1H-isomer (4) as well as to their anion (5) which is isoelectronic with [3.2.2]cycloazine (6)^[3].

According to quantum-chemical calculations by Zahradnik *et al.*^[4], the anion (5) containing twelve π -electrons should be electronically more stable than the corresponding cation. Rapoport *et al.*^[2] and Streitwieser Jr.^[6] postulated



that the acidity of 2aH-cyclopent[cd]indene (3) should be comparable with that of phenols. The 1H-tautomer (4) was not taken into account in these considerations.

In order to test these predictions experimentally we synthesized the lithium salt of (5). Rapoport *et al.*^[7] prepared

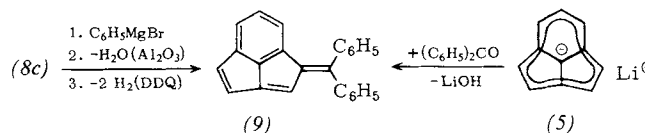
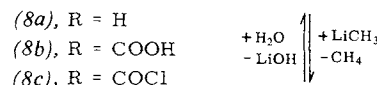
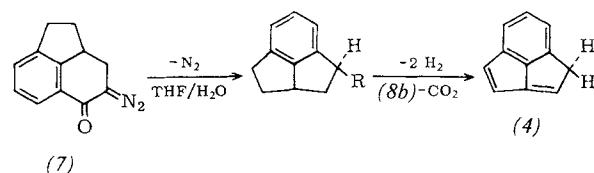
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the strained 2,2a,3,4-tetrahydrocyclopent[cd]indene (8a) and several of its derivatives by Pb salt distillation of 7-carboxy-1-indanacetic acid, but all attempts to introduce double bonds into (8) were unsuccessful.

By photolysis of 4-diazo-3,4-dihydro-5(2aH)acenaphthenone (7)^[8] in tetrahydrofuran/water (5:1) with a Hg high-pressure lamp (Q 81, Quarzlampen-Gesellschaft Hanau) we prepared 2,2a,3,4-tetrahydrocyclopent[cd]indene-1-carboxylic acid (8b)^[9] in 36% yield [colorless needles, m. p. 114°C; UV spectrum (in *n*-hexane): λ_{\max} = 217 (3.97), 269 (2.92), 276 (2.90) nm (log ϵ); NMR spectrum (in CCl₄): τ = -2.42 (1 H/s), 2.30—2.80 (3 H/m), 5.50 (1 H/dd, J = 5 Hz and J = 11 Hz), 6.30—8.50 (7 H/m)].

The acid (8b) can be dehydrogenated, with simultaneous decarboxylation, in the gas phase by 10% palladized charcoal at 480°C in a high vacuum; the hydrocarbon (4) produced was isolated at -70°C and, after chromatography on Al₂O₃ (activity 3, neutral) at -10°C, was



obtained in 40% yield as a pale yellow oil that solidified at 0°C and was very sensitive to autoxidation. The UV spectrum of (4) in *n*-hexane [λ_{\max} = 251 (4.11), 254 (4.11), 273 (3.65), 309 (3.54), 316 (3.64), 330 (3.60) nm (log ϵ)] is similar to that of 1-isopropylideneindene^[10]. The NMR spectrum of (4) (in CCl₄) contains, besides a resolved doublet (J = 1.5 Hz) centered at τ = 6.07 for the methylene protons at position 1, two multiplets centered at τ = 3.38 (2 H) and τ = 2.80 (4 H) due to the six further protons. The exclusive formation of (4) by the dehydrogenation of (8b)—the tautomer (3) could not be observed in the product—shows that the fulvenoid hydrocarbon (4) has an energy content lower than that of its tautomer 2aH-cyclopent[cd]indene (3). Attempts to prepare the 1-carboxylic acid of (4) directly by Wolff rearrangement of 4-diazo-5(4H)-acenaphthylenone^[11] have so far been unsuccessful.

Contrary to expectation, 1H-cyclopent[cd]indene (4) cannot be converted into its anion (5) either by methanolic NaOH or by sodium methoxide in methanol. However, treating (4) with methyllithium in tetrahydrofuran/ether (2:1) at -30°C afforded the lithium salt of (5) as a thermally not very stable, red-orange compound, sensitive to autoxidation and hydrolysis, which was precipitated in crystalline form by *n*-hexane. The position and intensity of the long-wave band in the UV spectrum of the Li salt of (5) [in THF/ether (20:1) at -30°C^[12], λ_{\max} = 338 (3.58), 346 (3.58), 354 (3.60), 458 (2.88) nm (log ϵ)] are in good agreement with SCF—CI calculations^[14]. The NMR

spectrum (in THF at -55°C) shows, besides the two doublets of the two AB systems of the five-ring protons at $\tau = 3.15$ (H-2, H-3) and 3.65 (H-1, H-4) ($J = 4.0$ Hz), also a multiplet centered at $\tau = 2.70$ for the three six-ring protons. Hydrolysis of (5), which regenerates (4), also confirms the theoretical expectations^[4], according to which position 1 or 4 should have a high electron density. In agreement therewith, reaction of (5) with benzophenone leads to thermally stable 1-(diphenylmethylene)cyclopent[cd]indene (9) [yellowish-orange prisms, m. p. 125°C (dec); UV spectrum (in *n*-hexane), $\lambda_{\text{max}} = 255$ (4.34), 310 (4.35), 352 (4.28) nm (log ϵ); NMR spectrum (in CCl_4), $\tau = 2.62$ (6 H/s), 2.66 (3 H/s), 2.70—3.70 (7 H/m)], which can also be obtained from (8c)^[13] and phenylmagnesium bromide after subsequent dehydration and by dehydrogenation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in 30% yield.

Like the formation of (4) from (8b), the hydrolysis of the Li salt of (5) which leads to (4) shows that (4) is energetically favored over (3). Correspondingly, a higher total π electron energy was found by SCF—CI calculations^[14] for the 1*H*-tautomer (4) than for the 2*aH*-tautomer (3)^[15]. The unexpectedly low acidity of (4), comparable with that of indene, probably represents a considerable difference of 1*H*-cyclopent[cd]indene (4) from its 2*aH*-tautomer (3) for which a p*K* value of 11 has been calculated^[6]. This can probably be ascribed to a considerably lower gain of energy on conversion of the fulvenoid tricycle (4) into its anion (5) than in the corresponding deprotonation of the indene-like hydrocarbon. Also, the correlation obtained by Streitwieser's method between acidity and the π -electron energy difference of anion and hydrocarbon leads to an appreciably lower p*K* value for (4) than for (3). Attempts to convert the hydrocarbon (4) into its cation and radical are in progress.

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[8] (7) was obtained by M. O. Forster's method (J. Chem. Soc. 107, 260 (1915)) from 3,4-dihydro-4-(hydroxyimino)-5(2*aH*)-acenaphthenone [7] and chloramine as pale yellow, small, light-sensitive rods, m. p. 61°C , in 75% yield.

[9] All the compounds described gave correct analyses.

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[11] Prepared from 4-amino-5-acenaphthenol hydrochloride (H. Rapoport, T. P. King, and J. B. Lavigne, J. Amer. Chem. Soc. 73, 2718 (1951)) and *n*-butyl nitrite; on recrystallization from light petroleum in presence of active charcoal the 4-diazo-5(4*H*)-acenaphthenone first obtained in this synthesis was dehydrogenated to the acenaphthylene derivative; pale yellow needles, m. p. 134°C ; yield 56%.

[12] The mean errors in the extinctions, referred to 20°C , in the UV spectrum of the Li salt of (5) amount to 5—10%. For UV measure-

ments a solution containing methyl lithium was used whose low transmittance below 330 nm did not permit the absorption curve to be observed at lower wavelengths.

[13] Prepared from (8b) and thionyl chloride.

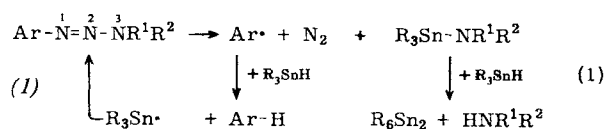
[14] R. Zahradnik, personal communication.

[15] Simpler HMO calculations for (3) and (4) led to the same result (A. Streitwieser, J. I. Brauman, and C. A. Coulson: Supplement Tables of Molecular Orbital Calculations. Pergamon Press, Oxford 1965; E. Heilbronner and P. A. Straub: HMO Hückel Molecular Orbitals. Springer-Verlag, Berlin—Heidelberg—New York 1966).

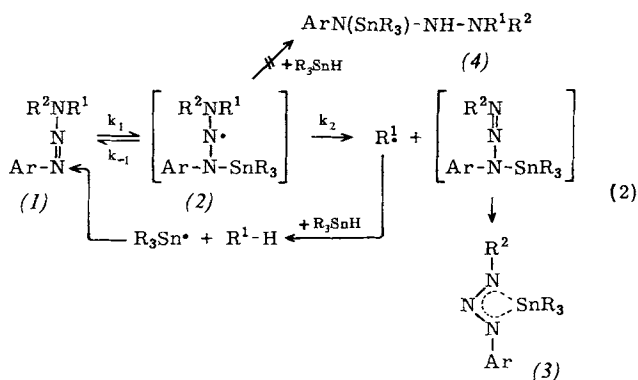
Free-Radical $\text{S}_{\text{H}2\gamma}$ Displacement in the Triazene System^[**]

By Jochen Hollaender and Wilhelm P. Neumann^[*]

The action of stannyl radicals $\text{R}_3\text{Sn}^{\bullet}$ on 1-aryl-3-alkyl-triazenes (1*a*)—(1*c*) resulted in replacement of the arylazo group on N^3 by the stannyl group [eq. (1) and Table]. This $\text{S}_{\text{H}2\alpha}$ reaction corresponds to known types of displacement by free radicals^[2-5].



Surprisingly, 1,3-displacement ($\text{S}_{\text{H}2\gamma}$) also occurs and predominates or becomes almost the only reaction when at least one of the groups R^1 and R^2 on N^3 forms a stable



free radical, *i. e.* when the dissociation energy of its bond to N^3 is lowered. Examples include $\text{R}^1 = \text{benzyl}$, triphenylmethyl, or trialkylstannyl [see (1*d*)—(1*i*), eq. (2), and Table]. The stannyl radical attacks at N^1 . The intermediate

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