		Yi	Yield (%)		
Olehn	Azidoaikane		[b]	[c]	
Styrene	1,4-Diazido-2,3-diphenylbutane	57		55	
α-Methylstyrene	1,4-Diazido-2,3-dimethyl- 2,3-diphenylbutane	45		43	
Cyclooctene	1,2-Diazidocyclooctane Azidocyclooctane 3-Azido-1-cyclooctene	24		15 17	
1-Octene	1,2-Diazidooctane 1-Azidooctane 1-Azido-2-octene 3-Azido-1-octene	17	18	3 3 3	
Cyclohexene	1,2-Diazidocyclohexane 3-Azido-1-cyclohexene Azidocyclohexane	18		5 10	
l,1-Diphenyl- ethylene	1,2-Diazido-1,1-diphenylethane 2-Azido-1,1-diphenylethyl acetate	15 33			

[a] Yield of azide referred to current consumption.

[b] Yield of azide referred to starting amount of olefin.

[c] Yield of amine, referred to current consumption, after reductive elimination of nitrogen.

1,4-Diazido- and 1,4-Diamino-2,3-dimethyl-2,3-diphenylbutane

A solution of sodium azide (12 g) and  $\alpha$ -methylstyrene (50 ml, 43 g) in glacial acetic acid is electrolyzed at 40 °C using an anode potential of +1.6 V (against Ag/AgCl) controlled by a potentiostat and a current density of 30 mA/cm<sup>-2</sup> at platinum electrodes in a cell without diaphragm until consumption of 0.150 Faraday. The solution is then poured into water (200 ml), extracted with ether, and the ethereal phase is washed with dilute sodium hydroxide until neutral and then dried over sodium sulfate. After distilling off the ether and excess  $\alpha$ -methylstyrene there remains 21.0 g of crude product. 0.41 g of the diazide can be separated from 0.8 g of the crude product by preparative thin layer chromatography using benzene/ petroleum ether (40-60 °C) (1 : 1 v/v) as eluent. 5.6 g of the crude product is hydrogenated in methanol with Raney-Ni/ hydrogen to give 2.3 g of the diamine (b.p. 160–165  $^{\circ}C/0.01$ torr). The structures are confirmed by C, H, N-analysis, molecular weight, IR-, NMR-, and mass spectra.

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## Cycloadditions to the Azulene System

## By K. Hafner, J. Häring, and W. Jäkel<sup>[\*]</sup>

Cycloadditions to the azulene system have not hitherto been observed. Instead, azulene reacts, *e.g.*, with maleic anhydride *via* an "addition-substitution route" to give 1-azulenylsuc-



(a),  $R = R^1 = C_6 H_5$ (b),  $R - R^1 = (CH_2)_6$ 

Com- pound	M.p. (°C)	UV $\lambda_{\max}$ (nm) (log $\varepsilon$ ) (in <i>n</i> -hexane)	NMR (τ) [a]
(1),	158-159 blue scales (ligroin)	298 (4.67), 376 (3.79), 561 (2.69), 607 (2.56), 668 (2.07)	0.60 (H-4/s), 1.80 (H-8/d; $J = 10$ Hz), 1.97 (H-1, H-3/m), 2.20 (H-2/t; $J = 4$ Hz), 2.60 (H-7/d; J = 10 Hz), 2.40-2.65 (C <sub>6</sub> H <sub>5</sub> /m) (CDCl <sub>3</sub> )
(2b)	126 yellow crystals (pet. ether)	231 (4.16), 269 (4.01), 318 (3.51), 404 (2.75)	2.42 (C <sub>6</sub> H <sub>5</sub> /m), 3.24 (1 H/m), 4.02 (3 H/m), 4.50 (1 H/s), 5.55 (1 H/d; $J = 8$ Hz), 7.34–8.92 (-(CH <sub>2</sub> ) <sub>6</sub> -/m) (CCl <sub>4</sub> )
(3a)	138-139 blue crystals (ligroin)	248 (4.26), 292 (4.78), 338 (3.75), 352 (3.85), 590 (2.66), 612 (2.65), 643 (2.65), 713 (2.28)	1.49 (H-4/s), 1.70 (H-8/d; $J = 10$ Hz), 2.10 (H-2/t; J = 4 Hz), 2.63 (H-1, H-3/d; $J = 4$ Hz), 2.75 (H-7/d; J = 10 Hz), 2.89 (2C <sub>6</sub> H <sub>5</sub> /s) (CDCl <sub>3</sub> )
(3b)	56 blue platelets (pet. ether)	240 (4.17), 281 (4.80), 287 (4.77), 301 (3.98), 322 (3.37), 330 (3.51), 333 (3.59), 345 (3.69), 349 (3.79), 361 (3.08), 580 (2.54), 601 (2.52), 632 (2.53), 662 (2.26), 700 (2.23)	1.83 (H-4/s), 1.95 (H-8/d; $J = 10$ Hz), 2.30 (H-2/t; J = 4 Hz), 2.87 (H-1, H-3/d; $J = 4$ Hz), 3.04 (H-7/d; J = 10 Hz), 6.83–7.17 (-(CH <sub>2</sub> ) <sub>2</sub> -/m), 7.93–8.80 (-(CH <sub>2</sub> ) <sub>4</sub> -/m) (CCI <sub>4</sub> )
(5a)	201-202 blue crystals (ligroin)	245 (4.41), 295 (4.79), 337 (3.74), 353 (4.81), 588 (2.73), 608 (2.71), 642 (2.70), 708 (2.32)	1.59 (H-8/d; $J = 10$ Hz), 2.21 (H-2/t; $J = 4$ Hz) 2.55 (H-1, H-3/m), 2.69 (H-7/d; $J = 10$ Hz) 2.88 (C <sub>6</sub> H <sub>5</sub> /s), 2.94 (C <sub>6</sub> H <sub>5</sub> /s), 3.24 (C <sub>6</sub> H <sub>5</sub> /s) (CDCl <sub>3</sub> )
(5b)	78 blue platelets (pet. ether)	251 (4.41), 289 (4.75), 293 (4.76), 297 (4.75), 339 (3.63), 349 (3.73), 353 (3.78), 365 (3.29), 582 (2.68), 605 (2.66), 635 (2.64), 703 (2.27)	2.00 (H-8/d; $J = 10$ Hz), 2.31 (H-2/t; $J = 4$ Hz), 2.72 (H-1, H-3/m), 2.75 (C <sub>6</sub> H <sub>5</sub> / <sub>8</sub> ), 3.09 (H-7/d; $J = 10$ Hz) 6.32-8.97 (-(CH <sub>2</sub> ) <sub>6</sub> -/m) (CCl <sub>4</sub> )

[a] TMS as internal standard.

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Hafner, Klaus: Cycloadditions to the Azulene System aus Angewandte Chemie international Edition 9, Jahrgang 1970, Nr. 2 Copyright © 1970 Wiley by Verlag Chemie, GmbH, Germany cinic anhydride and with tetracyanoethylene to yield 1-tracyanovinylazulene<sup>[1]</sup>.

In contrast, the 5-azaazulene system <sup>[2]</sup> is able to enter into cycloadditions with alkynes, the heterocycle undergoing simple conversion into previously inaccessible derivatives of carbocyclic azulene. 6-Phenyl-5-azaazulene (1)<sup>[3]</sup> reacts with an excess of tolan at 350 °C to give 30% of 5,6-diphenyl-azulene (3a)<sup>[4]</sup> and benzonitrile, as well as 5% of 4,5,6-triphenylazulene (5a) and hydrocyanic acid. Formation of (3a) and (5a) would suggest the intermediacy of the 1,4 adducts (2a) and (4a) and their Alder-Rickert cleavage to the carbocyclic azulene. Disrotatory thermal valence isomerization of (1) to (7) and (8), which is forbidden by the Woodward-Hoffmann rules<sup>[5]</sup>, and subsequent elimination of benzonitrile or hydrocyanic acid to give the pentalenes (9) and (10), respectively, which could also react with tolan to give (3a) and (5a)<sup>[6]</sup>, was ruled out by experimental findings<sup>[3]</sup>:



1-Methyl-6-phenyl-5-azaazulene and 4-methyl-6-phenyl-5azaazulene give different azulenes with tolan. If the reaction sequence  $(1) \rightarrow (7) \rightarrow (9)$  were to apply, then both azaazulenes would give 1-methylpentalene and thus either the same methyldiphenylazulene or an identical mixture of isomers.

Evidence for 1,4-adduct formation during reaction of (1) with acetylenes comes from the reaction of (1) with cyclooctyne<sup>[7]</sup> in the molar ratio 1:4 at 170 °C (reaction time: 15 s). From the reaction mixture a 25% yield of the 1,4 adduct (2b) can be isolated, whose Alder-Rickert cleavage (250 °C; 30 s) affords 5,6,7,8,9,10-hexahydrocycloocta[f]azulene(3b)(60%) and a minor amount of 3-phenyl-5,6,7,8,9,-10-hexahydrocycloocta[c]pyridine (6b). The strained adduct (4b) was also expected but, unlike (2b), decomposes to 6 phenyl-7,8,9,10,11,12-hexahydrocycloocta[e]azulene (5b) (30%) under the reaction conditions.

The hetero atom in the seven-membered ring of the 5-azaazulene system alters the electron distribution and reduces the  $\pi$ -electron delocalization compared with the azulene system<sup>[8]</sup>. This effect is probably responsible for the 1,4 addition of the  $\alpha,\beta$ -unsaturated azomethine partial structure in (1) to the alkynes. The reaction may proceed via a Diels-Alder reaction "with inverse electron demands" <sup>[9]</sup> or as a two-step cycloaddition. Decomposition of the 1,4 adducts (2) and (4) to carbocyclic azulene derivatives and pyridine profits from the energy gain involved in formation of the cyclic conjugated systems.

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## Metal-Ligand Bonding in Sulfinato Complexes of Transition Metals

By E. Lindner, G. Vitzthum, D. Langner, and I.-P. Lorenz<sup>[\*]</sup>

Bis- and tris(sulfinato) complexes are formed in the reaction of sodium sulfinates with soluble compounds of divalent and trivalent transitions metals in water or alcohol:

$$n \operatorname{RSO}_2\operatorname{Na} + \operatorname{MX}_n \rightarrow \operatorname{M}(\operatorname{SO}_2\operatorname{R})_n + n \operatorname{NaX}$$
 (1)  
(1)-(5)

(X = halogen, acetate)

R	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	СН3
$(n = 2) \mathbb{Z}n$	(1a)	(1b)	(1c)
Cd	(2a)	(26)	
Hg	(3a)	(3b)	(3c)
(n = 3) Cr	(4a)	(4b)	(4c)
Fe	(5a)	(Sb)	(5c)

The toluene- and benzenesulfinato complexes of zinc, cadmium<sup>[1]</sup>, and mercury<sup>[2]</sup> (1a)—(3b) have already been described. We have now succeeded in preparing bis(methanesulfinato)mercury (3c) and -zinc (1c) as the S-type.

Apart from the anhydrous mercury compounds (3a) and (3b)<sup>[3]</sup>, little has been known about the structure of the complexes (1a)-(2b) except that the  $RSO_2^-$  ligands are linked to  $M^{2+}$  via oxygen.

We have now found that the type of bonding of the ligands to the metal ion in (1a)-(3b) is particularly dependent on the water content of the compounds.

The benzene- and methanesulfinato complexes (1b), (2b), (3b), and (3c) prepared in water at room temperature are