| Olefin | Azidoalkane | Yield (\%) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | [a] | [b] | [c] |
| Styrene | 1,4-Diazido-2,3-diphenylbutane | 57 |  | 55 |
| $x$-Methylstyrene | 1,4-Diazido-2,3-dimethyl-2,3-diphenylbutane | 45 |  | 43 |
| Cyclooctene | 1,2-Diazidocyclooctane <br> Azidocyclooctane <br> 3-Azido-1-cyclooctene | 24 |  | $\begin{aligned} & 15 \\ & 17 \end{aligned}$ |
| 1-Octene | 1,2-Diazidooctane <br> 1-Azidooctane <br> 1-Azido-2-octene <br> 3-Azido-1-octene | 17 | 18 | 3 3 3 |
| Cyclohexene | 1,2-Diazidocyclohexane <br> 3-Azido-1-cyclohexene <br> Azidocyclohexane | 18 |  | 5 10 |
| 1,1-Diphenylethylene | 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 $40^{\circ} \mathrm{C}$ using an anode potential of +1.6 V (against $\mathrm{Ag} / \mathrm{AgCl}$ ) controlled by a potentiostat and a current density of $30 \mathrm{~mA} / \mathrm{cm}^{-2}$ at platinum electrodes in a cell without diaphragm until consumption of 0.150 Faraday. The solution is then poured into water ( 200 $\mathrm{mI})$, 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 $\left(40-60^{\circ} \mathrm{C}\right)(1: 1 \mathrm{v} / \mathrm{v})$ 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. $160-165^{\circ} \mathrm{C} / 0.01$ torr). The structures are confirmed by $\mathrm{C}, \mathrm{H}, \mathrm{N}$-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 [*]
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), $\mathrm{R}=\mathrm{R}^{1}=\mathrm{C}_{6} \mathrm{H}_{5}$
(b), $\mathrm{R}-\mathrm{R}^{1}=\left(\mathrm{CH}_{2}\right)_{6}$

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

[a] TMS as internal standard.
cinic anhydride and with tetracyanoethylene to yield 1-trccyanovinylazulene ${ }^{[1]}$.
In contrast, the 5 -azaazulene system ${ }^{[2]}$ 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) ${ }^{[3]}$ reacts with an excess of tolan at $350^{\circ} \mathrm{C}$ to give $30 \%$ of 5,6 -diphenylazulene ( $3 a)^{[4]}$ and benzonitrile, as well as $5 \%$ of $4,5,6$-triphenylazulene ( $5 a$ ) and hydrocyanic acid. Formation of ( $3 a$ ) and ( $5 a$ ) 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 WoodwardHoffmann rules ${ }^{[5]}$, 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) [6], was ruled out by experimental findings ${ }^{\text {[3] }}$ :


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 ${ }^{[7]}$ in the molar ratio $1: 4$ at $170^{\circ} \mathrm{C}$ (reaction time: 15 s ). From the reaction mixture a $25 \%$ yield of the 1,4 adduct ( $2 b$ ) can be isolated, whose Alder-Rickert cleavage $\left(250^{\circ} \mathrm{C}\right.$; 30 s ) affords $5,6,7,8,9,10$-hexahydrocycloocta[f]azulene ( $3 b$ ) ( $60 \%$ ) and a minor amount of 3-phenyl-5,6,7,8,9,10 -hexahydrocycloocta $[c]$ pyridine ( $6 b$ ). The strained adduct (4b) was also expected but, unlike ( $2 b$ ), 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 ${ }^{[81}$. 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" $[9]$ 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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\begin{array}{lr}
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\end{array}
$$

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

By E. Lindner, G. Vitzthum, D. Langner, and I.-P. Lorenz [*]
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:

$$
\left.\begin{array}{rl}
n \mathrm{RSO}_{2} \mathrm{Na}+\mathrm{MXX}_{n} \rightarrow \begin{array}{c}
\mathrm{M}\left(\mathrm{SO}_{2} \mathrm{R}\right)_{n}+n \mathrm{NaX} \\
(1)-(5)
\end{array} \\
(\mathrm{X}=\text { halogen, acetate) }
\end{array}\right)
$$

The toluene- and benzenesulfinato complexes of zinc, cadmium ${ }^{[1]}$, and mercury ${ }^{[2]}$ ( $1 a$ )-(3b) have already been described. We have now succeeded in preparing bis(methanesulfinato) mercury ( $3 c$ ) and -zinc ( $I c$ ) as the $S$-type.
Apart from the anhydrous mercury compounds (3a) and (3b) ${ }^{[31}$, little has been known about the structure of the complexes ( $1 a$ )-(2b) except that the $\mathrm{RSO}_{2}-$ Iigands are linked to $\mathrm{M}^{2+}$ via oxygen.
We have now found that the type of bonding of the ligands to the metal ion in (la)-(3b) is particularly dependent on the water content of the compounds.
The benzene- and methanesulfinato complexes ( 16 ), ( $2 b$ ), $(3 b)$, and (3c) prepared in water at room temperature are

