

rotary evaporator. 100 ml of water was added to the residue, the solution was extracted with 400 ml of ether, and the extract was dried over magnesium sulfate. Small quantities of 2-(diphenylhydroxymethyl)-4,5,5-triphenyloxazoline crystallized out on standing, and this was filtered off. Removal of the ether under vacuum left 13.3 g of residue. 3.5 g of this was chromatographed on 300 g of silica gel. 2.5 g (74%) of 1,1,2-triphenylethylene could be eluted with chloroform.

α -Methylstyrene:

Starting from methyl isocyanide and butyllithium, 50 mmole of isocyano-methylolithium was prepared at -70°C (analogously to the above procedure). To the suspension was added with stirring at -70°C 6.0 g (50 mmole) of acetophenone. The mixture was refluxed (under nitrogen) for 40 hours and subsequently poured into 600 ml of water. The olefin was extracted five times with 100-ml portions of pentane and dried over magnesium sulfate. The usual workup yielded 3.8 g of α -methylstyrene with b.p. $60-61^{\circ}\text{C}/18$ torr.

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[*] Prof. Dr. U. Schöllkopf and Dr. F. Gerhart
Organisch-Chemisches Institut der Universität
34 Göttingen, Windausweg 2 (Germany)

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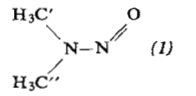
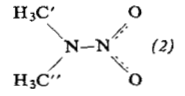
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Structure of Nitroso- and Nitro-dimethylamine

By P. Rademacher[*], R. Stølevik[**], and W. Lüttke[*]

Dedicated to Professor H. Brockmann on the occasion of his 65th birthday

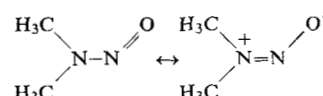
Continuing our systematic study of donor-acceptor molecules D-A, we have determined the structure of molecules of medium size containing an electron donor D linked directly to an electron acceptor A; we have used electron diffraction, IR, Raman, and NMR measurements as well as quantum-mechanical calculations. The structure recently published^[1] for dimethylnitrosoaminecopper(II) chloride $(\text{CH}_3)_2\text{N}-\text{NOCuCl}_2$ induced us to report our results for the molecular geometry of nitrosodimethylamine (1) and nitrodimethylamine (2).

		
Symmetry	C_s	C_{2v}
Bond lengths (Å):		
N-O	1.235 (2)	1.223 (2)
N-N	1.344 (2)	1.382 (3)
C-N	1.461 (2)	1.460 (3)
C-H	1.129 (3)	1.121 (5)
Bond angles ($^{\circ}$):		
N-N-O	113.6 (2)	114.8 (7)
O-N-O		130.4 (1.3)
C'-N-N	120.3 (3)	116.2 (3)
C''-N-N	116.4 (3)	116.2 (3)
N-C-H	109.6 (8)	101.9 (1.9)

Electron diffraction of (1) and (2) was measured in the usual way^[2]. The molecular parameters (bond distances, angles, root mean squares of the vibrational amplitudes, shrinkage parameters) were determined from the scattering intensity curves by the method of least squares. No significant deviation from a planar skeleton was indicated for either molecule; and this finding was supported by quantum-chemical calculations and spectroscopic measurements^[3].

The following results (standard deviations in parentheses) were obtained for the molecular geometries:

In a comparison of the structural data for gaseous (1) with those for the molecule bound in the CuCl_2 complex (3)^[1] it is remarkable that both have the same C-N bond length, but that the N-N and the N-O bonds of the ligand in the complex are appreciably shorter (by 0.08 and 0.02 Å, respectively) while the N-N-O and the C'-N-N angles are larger (by about 4°). The greatest shortening from the free molecule (1) to (3) occurs with the N-N bond length, which indicates an electronic influence of the type



in which the influence of the dimethylamino group on the nitroso group strengthens the complex bonding in the sense that the ligand becomes more firmly attached to the central atom. The compound (1) differs sharply from azomethane in this respect, since the molecular dimensions of azomethane are the same in the gaseous state^[4] as when a ligand in the CuCl_2 complex^[5].

The difference in the N-N distances for (1) and (2) (0.04 Å) can be interpreted as showing that the dimethylamino group is a stronger electron acceptor than the nitro group.

A detailed report of the electron diffraction study will appear elsewhere shortly^[6].

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[*] Dipl.-Chem. P. Rademacher and Prof. Dr. W. Lüttke
Organisch-Chemisches Institut der Universität
34 Göttingen, Windausweg 2 (Germany)

[**] R. Stølevik
Universitetet i Oslo, Kjemisk Institutt
Blindern, Oslo 3 (Norway)

[1] U. Klement and A. Schmidpeter, *Angew. Chem.* 80, 444 (1968); *Angew. Chem. internat. Edit.* 7, 470 (1968). In Fig. 1 of the German version of this paper the value of the Cu-O distance was given erroneously as 2.82 instead of 2.28 Å. Editorial correction.

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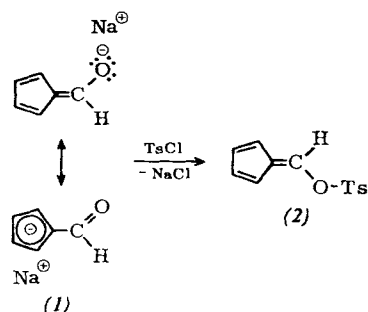
A Simple Synthesis of Substituted Fulvenes from 6-Fulvenyl *p*-Toluenesulfonates

By K. Hafner, W. Bauer, and G. Schulz[*]

6-Dimethylaminofulvene^[1] and its derivatives are useful starting materials for the preparation of non-benzenoid, cyclic, conjugated π -electron systems^[2]. In the treatment of 6-fulvenyl *p*-toluenesulfonates with nucleophilic reagents we have found a simple process for the introduction of functional groups at the 6-position of the fulvenoid system.

While reaction of sodium formylpentadienide (1)^[3] with the Vilsmeier complex from dimethylformamide and dimethyl

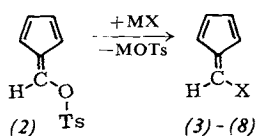
sulfate^[4] or with carbon dioxide affords 6-dimethylamino-fulvene-2-carbaldehyde or 6-hydroxyfulvene-2-carboxylic acid, respectively, by C-acylation, we observed formation of O-acylation products^[5] in the reaction with acyl halides. *p*-Toluenesulfonyl chloride and (1) in ether at -5 °C give



6-fulvenyl *p*-toluenesulfonate (2) [yield 60%; yellow needles (from ether), decomp. 47–48 °C; UV spectrum (*n*-hexane), $\lambda_{\max} = 226 \text{ nm}$ ($\log \epsilon = 4.11$), 261 (4.34), 358 (2.51); NMR spectrum (CCl_4), $\tau = 2.25$ (2H), d, $\tau = 2.70$ (3H), d, $\tau = 3.80$ (4H), m, $\tau = 7.64$ (3H), s].

Analogously sodium 1-formylindenide and potassium 9-formylfluorene^[6] afford, respectively, 1-indenylidene methyl *p*-toluenesulfonate (benzofulvenyl *p*-toluenesulfonate) [yield 63%; pale yellow leaflets (from ethanol), m.p. 97–99 °C; UV spectrum (*n*-hexane), $\lambda_{\max} = 227 \text{ nm}$ ($\log \epsilon = 4.53$), 305 (3.82), 314 (3.90), 326 (4.79); NMR spectrum (CDCl_3), $\tau = 2.75$ (1H), m, $\tau = 7.67$ (3H), s] and 9-fluorenylidene methyl *p*-toluenesulfonate (dibenzofulvenyl *p*-toluenesulfonate) [yield 50%; pale yellow crystals (from ethanol), m.p. 103–105 °C; UV spectrum (*n*-hexane), $\lambda_{\max} = 223 \text{ nm}$ ($\log \epsilon = 4.69$), 228 (4.71), 247 (4.47), 257 (4.72), 274 (4.18), 283 (4.19), 300 (4.12), 313 (4.15); NMR spectrum (CDCl_3), $\tau = 2.4$ (13H), m, $\tau = 7.65$ (3H), s^[7]].

6-Fulvenyl *p*-toluenesulfonate (2) reacts with secondary amines, alkoxides, carbanions, or sodium azide below 0 °C with C–O fission, presumably involving an addition-elimination mechanism, yielding the fulvenes (3)–(8) that are substituted at C-6.



Benzo and dibenzo derivatives of (2) react with nucleophilic reagents analogously to the parent compound. 1-Indenylidene methyl *p*-toluenesulfonate and sodium azide in aqueous methanol, acetonitrile, or acetone affords 1-indenylidene methyl azide (azidobenzofulvene) [yield 21%; pale yellow needles (from light petroleum), m.p. 76–78 °C (decomp.); UV spectrum (*n*-hexane), $\lambda_{\max} = 236 \text{ nm}$ ($\log \epsilon = 3.97$), 274 (4.40), 283 (4.49), 333 (4.25), 346 (4.12)]; and 9-fluorenylidene methyl *p*-toluenesulfonate affords the corresponding azide (azidodibenzofulvene)^[9] [yield 57%; yellow needles (from light petroleum), m.p. 88–90 °C (decomp.); UV spectrum (*n*-hexane), $\lambda_{\max} = 227 \text{ nm}$ ($\log \epsilon = 4.55$), 233 (4.60), 246 (4.43), 253 (4.47), 263 (4.59), 280 (3.99), 290 (4.14), 302 (4.22), 325 (4.41), 337 (4.36)].

6-Fulvenyl *p*-toluenesulfonate (2):

A solution of *p*-toluenesulfonyl chloride (16 g) in ether (150 ml) is added dropwise to a suspension of sodium formylcyclopentadienide (1) (11.6 g) in ether (100 ml) at -5 °C with exclusion of oxygen and moisture. After 5 h the insoluble residue is filtered off under nitrogen, and the red ethereal solution is washed with water and dried over previously ignited Na_2SO_4 . The solvent is removed under nitrogen at reduced pressure and the red, oily residue is then chromatographed on Al_2O_3 (neutral, activity grade III) with ether, whereupon a yellow zone can be eluted. The eluate is concentrated under nitrogen and cooled to -50 °C. Compound (2) (15 g, 60%) is obtained as yellow needles that are sensitive to heat and to autoxidation and that decompose at 47–48 °C.

6-Fulvenyl azide (8):

A solution of sodium azide (6.5 g) in water (30 ml) is added to a solution of 6-fulvenyl *p*-toluenesulfonate (2) (12.8 g) in methanol (120 ml) at 0 °C, and the mixture is stirred for 4 h at -5 °C. After addition of water, the mixture is extracted with ether. The ether is removed under nitrogen at reduced pressure and the red, oily residue is chromatographed on Al_2O_3 (neutral, activity grade III) with light petroleum (40 to 60 °C). A red oil is obtained that affords 6-sulvenyl azide (8) (3 g, 50%), as a yellow-red compound that is crystalline up to about -40 °C, on condensation in a low-temperature trap. (8) decomposes at room temperature and is characterized by its photolabile nature and by its sensitivity to air.

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[*] Prof. Dr. K. Hafner, Dr. W. Bauer, and Dr. G. Schulz
Institut für Organische Chemie der Technischen Hochschule
61 Darmstadt, Schlossgartenstr. 2 (Germany)

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Compound	Metal	X	Yield (%)	M.p. (°C) B.p. (°C/torr)	UV (<i>n</i> -hexane) λ_{\max} (nm) (log ϵ)	NMR (τ)
(3)	K	(C_6H_5) CH_3N	51	65–66	336 (4.59)	2.45–2.9 (6H), m; 3.27–2.73 (4H), m; 6.38 (3H), s
(4)	K	(C_6H_5) $_2\text{N}$	39	95–96	301 (4.04) 351 (4.48)	2.4–2.98 (11H) m; 3.6–4.02 (3H), m; 5.0 (1H), m
(5)	K	1-Carbazolyl	28	99–101	236 (4.69) 286 (4.17) 371 (4.37)	1.9–2.92 (9H), m; 3.4–3.72 (4H), m
(6)	K	(CH_3) $_3\text{CO}$	20	60/10 ⁻³	280 (4.32) 284 (4.32) 349 (2.68)	3.0 (1H), s; 3.48–4.04 (4H), m; 8.6 (9H), s
(7) [8]	Li	C_6H_5				
(8)	Na	N_3	50	ca. -40	296 (4.44)	3.4 (1H), s; 3.5–4.0 (4H), m

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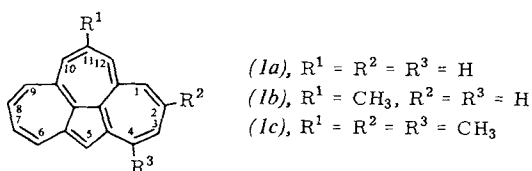
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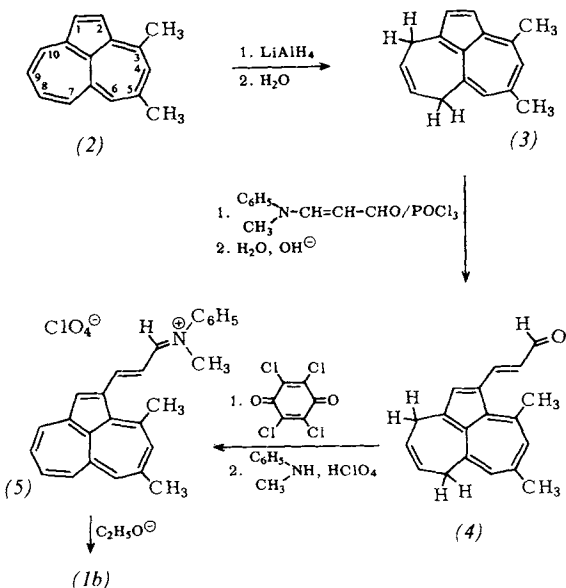
Azuleno[8,8a,1,2-def]heptalene

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



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*-methyl-anilino)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



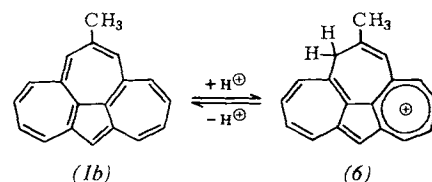
65–70% yield on partial reduction of (2) by $LiAlH_4$ in boiling tetrahydrofuran [dark blue crystals of m.p. 74–76 °C (from light petroleum)^[4]].

As a derivative of azulene, compound (3) is substituted exclusively at C-2 by electrophilic reagents. On reaction with 3-(*N*-methyl-anilino)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*-methyl-aniline 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 ($\log \epsilon = 4.40$), 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 $\tau = 5.46, 6.31, 6.04, \text{ and } 7.12$; 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 2*N* H_2SO_4 , leads to the reddish-violet conjugated acid (6) [UV spectrum of (1b) in CH_2Cl_2 /



CF_3COOH : $\lambda_{max} = 326$ nm ($\log \epsilon = 4.71$) 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 ($\equiv 12$), 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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