CHEMISTRY LETTERS, pp. 653-656, 1983. © The Chemical Society of Japan 1983

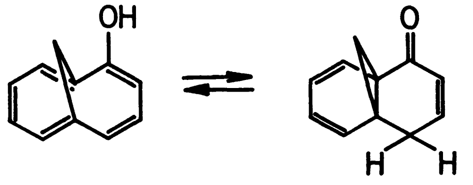
SYNTHESES OF A NEW CLASS OF DYES - COUPLING REACTIONS OF DIAZONIUM SALTS WITH 2- AND 3-ALKOXY-1,6-METHANO-[10]-ANNULENES

Richard NEIDLEIN,*[1] Christoph Martin RADKE,
and Reiner GOTTFRIED

Pharmazeutisch-Chemisches Institut
der Universitäten Karlsruhe (TH) und Heidelberg,
Im Neuenheimer Feld 364, D-6900 Heidelberg

2- and 3-Alkoxy-1,6-methano-[10]-annulenes were coupled with aryldiazonium salts yielding the corresponding quinone hydrazones as cycloheptatriene derivatives. Analytical data are discussed.

The hydroxy-1,6-methano-[10]-annulenes[2,3] 1 and 3 are iso-π-electronic with 1- and 2-naphthol. In solution they tautomerize partially to their keto isomers 2 and 4. By derivatization you can fix the aromatic state in 1[2,3] and 3 yielding the alkyl ethers 5 and 11. Reactions with diazonium salts ought to be possible - a consideration which led to the syntheses of the bridged quinone hydrazones 7a - 7c and 13/14a - c.



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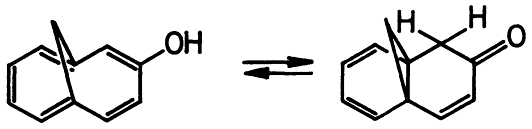

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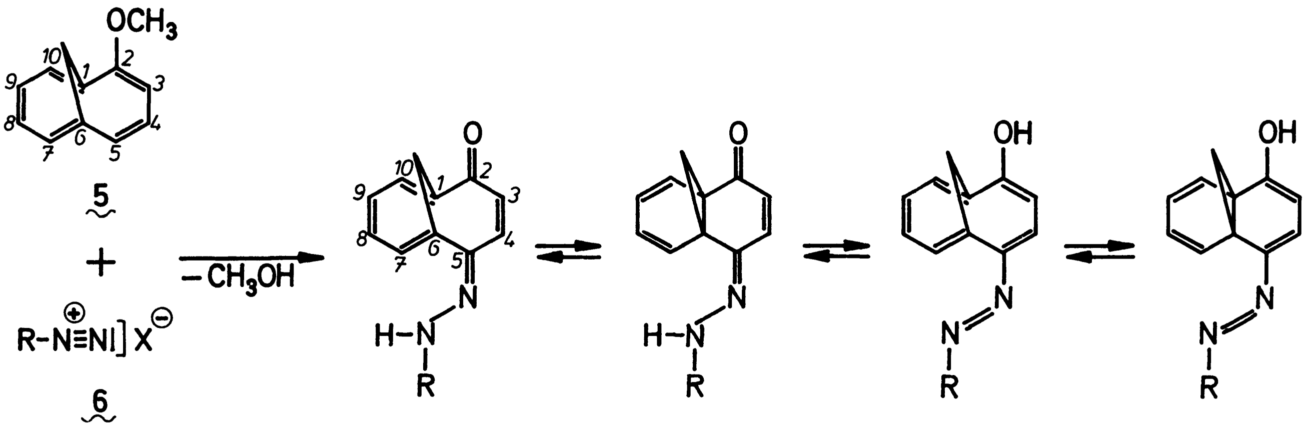

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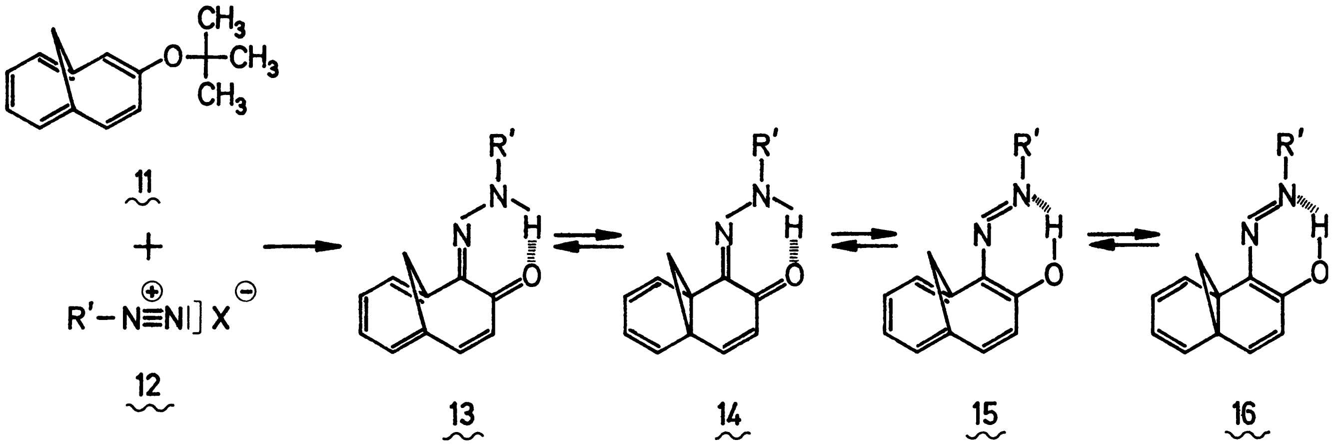
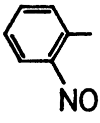
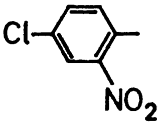
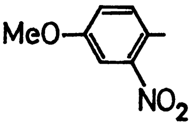
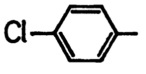
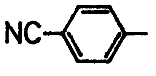
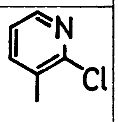


Table 1. Physical constants

7	a	b	c	13/14	a	b	c
R =				R' =			
Mp (°C):	138	177	165		165	189	153
yields (%):	36	69	27		78	<10	<10
UV/VIS(CH_2Cl_2):							
λ_{max} (nm)	441	450	480		468	443	438
lg ε	4.24	4.19	4.18		4.16	3.90	3.86

7a - c: A suspension of 3 mmoles of the diazonium salt in 5 ml acetic acid and 2 ml sulfuric acid is added to a solution of 3 mmoles of 5[4)] in 20 ml ether. The solid product is recrystallized from methyl ethyl ketone.

13/14a - c: A suspension of 5 mmoles of the diazonium salt in 8.75 ml acetic acid and 2.5 ml sulfuric acid is added to a solution of 5 mmoles 11 in 10 ml acetic acid. The mixture is neutralized and extracted with methylene chloride and the product purified by column chromatography and recrystallisation from acetone.

Satisfactory elemental analyses were obtained for all new compounds.

Table 2. ^{1}H-NMR data
(chemical shifts in ppm relative to TMS,
coupling constants J in Hz, solvent: $CDCl_3$)

	7 a	b	c	13/14 a	b	c
H-11	0.95 d	0.99 d	0.95 d	0.55 d	0.68 d	0.79 d
H-11'	3.66 d	3.60 d	3.58 d	2.62 d	2.58 d	2.72 d
$J_{11/11'}$	12.5	10.9	10.9	8.7	8.1	7.9
olefin.-	6.14 d	6.17 d	6.13 d	6.09 d	6.04 d	6.07 d
H	6.92 d	6.91 d	6.91 d	7.29 d	7.37 d	7.32 d
J	12.1	12.2	12.1	11.0	11.0	11.0
arom.-	6.9 -	6.9 -	6.8 -	6.6 -	6.5 -	6.5 -
H	7.3 m	7.3 m	7.3 m	7.2 m	7.2 m	7.2 m
N-H	12.28 s	12.19 s	12.19 s	14.63 s	14.31 s	14.43 s

Table 3. ^{13}C-NMR data (chemical shifts in ppm)

Compound	C-11	C-6	C-1	C-2	Solvent
7 a	33.0	109.9	116.8	191.3	CD_2Cl_2
b	32.6	109.7	116.5	191.0	$CDCl_3$
c	33.1	109.9	117.0	191.4	CD_2Cl_2
13/14 a	37.5	96.9	99.9	183.3	$CDCl_3$
b	36.7	89.2	91.8	184.3	"
c	36.6	89.2	91.8	184.0	"

Each of the new compounds may isomerize in two ways: The cycloheptatriene - norcaradiene and the hydroxy azo - quinone hydrazone equilibrium.

The NMR absorption of C-2 is typical for a carbonyl carbon. This clearly indicates that these dyes predominantly exist as quinone hydrazones. For the compounds 7a - c there is still further evidence: The IR spectra show a

N-H absorption at 3300 cm^{-1} whereas no OH absorption could be detected. Extensive NMR studies on the cycloheptatriene - norcaradiene equilibrium have been made by H. Günther and E. Vogel5,6). According to these publications there are two sensitive variables indicating the position of the equilibrium, the absorptions of C-1 and C-6 and the geminal coupling constants of the protons of C-11. The ^{13}C resonance absorptions range from about 115 ppm for the cycloheptatriene to 55 ppm for the pure norcaradiene isomers5). ^{1}H-NMR exhibits geminal coupling constants of about 11 Hz for the cycloheptatriene and 4.5 Hz for the norcaradiene tautomers. Taking these arguments in consideration the compounds 7a - c can clearly be identified as cycloheptatriene tautomers. For the compounds 13/14a - c both the absorptions of C-1 and C-6 and the geminal coupling constants for the methylene bridge protons are between those measured for the norcaradiene and the cycloheptatriene tautomers. For that reason we suggest that a fast equilibrium exists between 13a - c and 14a - c. Investigations on the temperature dependence of the equilibrium are planned. Hydrogen bonding between the hydrazone proton and the ortho nitro group is evident for the compounds 7a - c. Hofer and Uffmann7) give a hydrazone-^{1}H absorption of 11.8 to 12.0 ppm for 2-nitrophenyl hydrazones versus 9.0 to 10.0 ppm for hydrazones having no possibility to form hydrogen bonds. The assumption of hydrogen bonding between the hydrazone proton and the carbonyl group for the compounds 13/14a - c is confirmed by a work of M. Drew8). He measured N-^{1}H absorptions ranging from 15.09 to 15.89 ppm for phenylhydrazones of dimedone. The crystal structures of his products clearly indicate hydrogen bonding.

The new compounds described above were tested for their dyeing characteristics and have extinction coefficients comparable to those of the isoelectronic naphthoquinone dyes.

We thank the BASF AG, Bayer AG, Hoechst AG for chemicals and the Society of Chemical Industrie - Fonds der Chemie - and the Deutsche Forschungsgemeinschaft for special support of our research work.

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(Received February 15, 1983)