

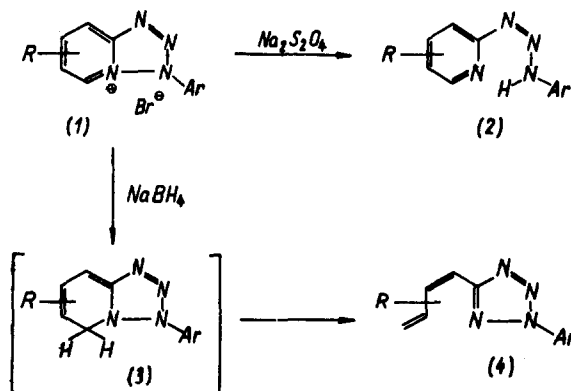
RING OPENINGS OF 3-ARYLTETRAZOLOPYRIDINIUM SALTS
 WITH NUCLEOPHILES: SYNTHESIS OF 1-(2-ARYL-5-TETRAZOLYL)-
 BUTADIENES, DIENE ETHERS AND DIENAMINES

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3-Aryltetrazolopyridinium salts (1) prepared¹ by cyclodehydrogenation of 1-(α -pyridyl)-3-aryltriazenes (2) react with aqueous sodium dithionite via opening of the tetrazole ring to afford the starting material (2) in nearly quantitative yield. We have found that with simple nucleophiles (sodium borohydride, morpholine, sodium methoxide) the pyridine instead of the tetrazole ring of 1 is cleaved, even under mild conditions, yielding butadiene derivatives that can be isolated in crystalline form.



3-Aryltetrazolopyridinium salts (1) with sodium borohydride in aqueous solution at room temperature (in DMF already at 0°C) give 1-cis-1-(2-aryl-5-tetrazolyl)-1,3-butadienes in good yields; e.g. 4a, where $Ar = p-CH_3O-C_6H_4$ and $R = H$ (m.p. 96°C), is obtained in 63%. Further derivatives (4b-f) are listed in Table 1. In order to prove that the tetrazole ring in 3-aryl-3,5-

dihydropyridotetrazole (3), formed as an intermediate via hydride attack, is subsequently rearomatized by the electrocyclic opening of its pyridine ring to give actually the cis-butadiene derivative, we have compared the NMR and UV spectra of the methyl derivatives of 4.

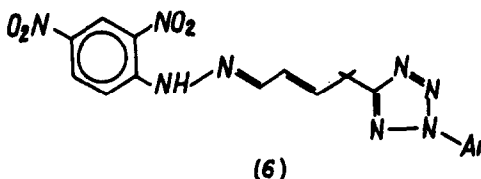
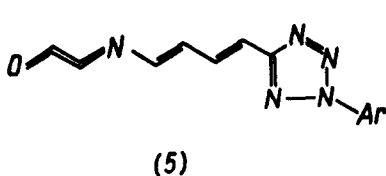
TABLE 1 (Ar = p-Cl-C₆H₄)

	<u>2</u>			<u>1</u>			<u>4</u>				
	R	M.p., °C	Yield %	R	M.p., °C	Yield %	R	M.p., °C	Yield %	UV (95 % EtOH) λ_m (log ϵ)	
f e c b	H	196	74	H	307	87	H	65	74	283(4.25)	253(4.31)
	3-CH ₃	167	57	8-CH ₃	242	76	1-CH ₃	96	68	285(sh)	262(4.52)
	4-CH ₃	209	64	7-CH ₃	294	81	2-CH ₃	125	80	286(4.36)	255(4.38)
	5-CH ₃	212	60	6-CH ₃	250	78	3-CH ₃	41	34	290(4.11)	263(4.42)
	6-CH ₃	154	46	5-CH ₃	303	61	4-CH ₃	108 ^x	50	288(4.22)	264(4.42)

^xM.p. is not sharp (102-8°C); the product is a mixture consisting of the 1-cis-3-trans and 1-cis-3-cis isomers.

The 1-(α -picolyl)-3-(4-chlorophenyl)triazenes (2c-f) have been prepared from the four 2-aminopicolines with 4-chlorophenyldiazonium chloride. Their cyclo-dehydrogenation gave the corresponding tetrazolopyridinium salts (1c-f), which were reduced with sodium borohydride to the methylbutadiene derivatives (4c-f).

The open-chain butadiene structure is proved by the characteristic parameters of the vinyl group: in 4e $\delta H_4 = 5.44$ ppm and $\delta H_4 = 5.54$ ppm (C₆D₆; $J_{4,4} = 1.9$ Hz) and in 4d $\delta H_3 = 7.83$ ppm (C₆D₆). The coupling constants of the ABX system of 4d calculated from these data are $J_{3,4} = 9.6$ Hz and $J_{3,4} = 17.8$ Hz; the parameters reproduce the spectrum of 4d very well. Finally, the cis structure of the dienes is proved by the fact that the coupling constants of H₁ and H₂ in 4e have the value of $J = 10.2$ Hz expected for the cis position. As the UV spectra of the remaining derivatives of 4 are analogous to that of 4d (cf. Table 1), the generalization of the cis structure is justified.

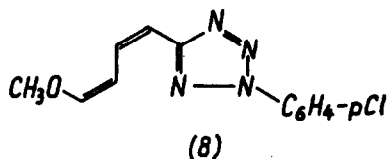
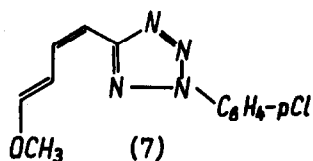


In the presence of secondary amines, e.g. morpholine (in methanol, at 0°C), it is again the pyridine ring of the salts 1 which is cleaved, whereas the tetrazole cycle remains intact. The product of these reactions, however, are not the cis- but the 1-trans-3-trans-1-(2-aryl-5-tetrazolyl)-4-morpholino 1,3-butadienes (5). Compounds 5a-c have a strong IR band at about 1620 cm^{-1} , characteristic of dienamines²; their UV spectra (Table 2) are different from those of cis-dienes (4); they give dinitrophenylhydrazones (6a-c) in good yield and undergo diene reaction with *N*-phenylmaleimide. It should be noted that, with the exception of 4c, cis compounds of the type 4 do not form Diels-Alder adducts even under drastic conditions.

TABLE 2

Ar	<u>5</u>			<u>6</u>	
	M.p., C	Yield, %	UV (95 % EtOH) λ_m (log ϵ)	M.p., C	Yield, %
<u>a</u> 4-CH ₃ O-C ₆ H ₄	128	53	355 (4.75) 247 (4.11)	186	80
<u>b</u> 4-Cl-C ₆ H ₄	161	61	327 (4.57) 262 (4.27)	202	54
<u>c</u> C ₆ H ₅	136	56	333 (4.66) 247 (4.11)	198	70

The reaction of salt 1b with sodium methoxide (in methanol, at 0°C) yields two diene derivatives, viz. 1-cis-3-trans-1-[2-(*p*-chlorophenyl)-5-tetrazolyl]-4-methoxy-1,3-butadiene (7; M.p. 162°C ; 29 %) and 1-cis-3-cis-1-[2-(*p*-chlorophenyl)-5-tetrazolyl]-4-methoxy-1,3-butadiene (8; M.p. 116°C ; 23 %). With dinitrophenylhydrazine, these diene ethers give the same phenylhydrazone as dienamine 5b, and their UV spectra are analogous to those of the 1-cis-dienes (4).



The remarkably strong tendency at low temperature of 3-aryltetrazolopyridinium salts (1) to ring opening with nucleophiles is presumably due to the positive charge of 1 and to the aromatic tetrazole structure of the products. This receives support from a comparison with known ring opening reactions of other fused ring systems. Some nitro and cyano derivatives of the neutral tetrazolopyridine have been found³ by the NMR method to undergo ring cleavage with alkali to give sodium tetrazolyldienolates; however, yields were not reported. The reaction with NaBH_4 of quinolizinium salts gave unsaturated quinolizidines, and the product of ring opening /pyridylbutadiene/ was isolated only in low yield even under drastic conditions⁴. Isoxazolopyridinium salts⁵ afford isoxazolinyldienamines, but this requires boiling with piperidine on a steam bath. Recently, quinolizinium salts⁶ have been reported to give dienamines in good yields but also under more drastic conditions, *viz.* boiling with morpholine.

Finally, the ambident reductive ring opening of 3-aryltetrazolopyridinium salts (1), leading in the presence of $\text{Na}_2\text{S}_2\text{O}_4$ to 2 and with NaBH_4 to 4, may be of interest as a new type of "charge- and orbital-controlled" reactions⁷.

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