N, N-DIALKYLDIAZENIUM BROMIDES IN THE DIENE SYNTHESIS

K. N. Zelenin and I. P. Bezhan

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 1, pp. 93–94, 1970

UDC 547.234'852

The diene synthesis with N, N-dialkyldiazenium bromides affords a method for the preparation of 1, 1-dialkyl-Δ^4-tetrahydropyridazinium salts.

N, N-Dialkyldiazenium salts (I) are obtained readily by the oxidation of unsymmetrical dialkylhydrazines in acid media [1]. Only two examples of the use of these compounds in the diene synthesis are known [2, 3]. Meanwhile, investigation of the reaction of I with 1, 3-dienes is of interest, both from the point of view of ascertaining their dienophilic activity, and as a method for the synthesis of 1, 1-dialkyl-Δ^4-tetrahydropyridazinium salts.

1, 1-Dialkyl-Δ^4-tetrahydropyridazinium Bromides

Compound II	R	R′	R″	R‴	R⁗	Mp, °C	Molecular formula	Found, %		Calculated, %		Yield, %
								N	Br	N	Br	
a	CH_3	H	H	H	H	188–190	$C_6H_{13}BrN_2$*	14.50 14.55	40.89 41.31	14.51	41.39	82
b	CH_3	H	CH_3	CH_3	H	181–183	$C_8H_{17}BrN_2$	12.54 12.63	36.05 36.12	12.67	36.14	72
c	CH_3	CH_3	H	H	CH_3	180	$C_8H_{17}BrN_2$**	12.49 12.42	36.67 36.70	12.67	36.14	95
d	C_2H_5	H	H	H	H	162–163	$C_8H_{17}BrN_2$	12.75 12.82	36.07 35.98	12.67	36.14	85
e	C_2H_5	CH_3	H	H	CH_3	124–125	$C_{10}H_{21}BrN_2$	11.14 11.30	32.44 32.50	11.24	32.07	80

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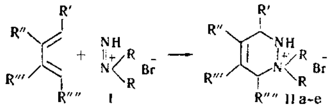
*Literature [2] mp 201-202° C, yield 73%.

**By analogy with literature data [5], probably the cis isomer.

We reacted dimethyl- and diethyldiazenium bromides with divinyl, trans-trans-1, 4- and 2, 3-dimethylbutadienes. The adducts obtained (II) were hygroscopic substances, readily soluble in alcohols and chloroform, but insoluble in solvents of low polarity.



The IR spectra of all the salts, in KBr discs (20 mg to 2 g of KBr), had bands of low intensity at 1655–1660 cm^{-1} (C=C), and high intensity bands at 3120–3150 cm^{-1} (NH). In compounds **IIa–IIc** there were bands at 2770 cm^{-1}, corresponding to the $(CH_3)_2\overset{+}{N}{}^4$ group, and all compounds except for **IIb** absorbed at 2980–3000 cm^{-1} ($H-\overset{|}{C}=\overset{|}{C}-H$). The NMR spectra (40 MHz, τ, 20% solutions in D_2O, 25° C, external standard HMDS): **IIa**, $(CH_3)_2\overset{+}{N}$ 6.32 singlet, NH—OH exchange 4.88 singlet, $H-C^3$ 5.87 multiplet, $H-C^{4,5}$ 3.56 multiplet, H—C 5.56 multiplet; **IIb**, $(CH_3)_2\overset{+}{N}$ 6.31 singlet, NH—OH exchange 4.90 singlet, $H-C^3$ 6.03 multiplet, $CH_3-C^{4,5}$ 7.92 singlet, $H-C^6$ 5.64 multiplet; **IIc** $(CH_3)_2\overset{+}{N}$ 6.31 (cis) singlet, 6.15 (trans) singlet, NH—OH 4.81 singlet, $H-C^3$ 5.69 multiplet, CH_3-C^3 8.28 doublet (J ~6 Hz), $H-C^{4,5}$ 3.60 multiplet, $H-C^6$ 5.56 multiplet, CH_3-C^6 8.14 doublet (J ~6 Hz).

Thus, the ability to undergo the diene synthesis reaction is a general property of all the 1, 1-dialkyldiazenium bromides examined, and provides a convenient method for obtaining quaternary salts of Δ^4-tetrahydropyridazine.

EXPERIMENTAL

1,1-Dialkyl-Δ^4-tetrahydropyridazinium bromides (II). A mixture of 0.2 mole of freshly prepared I [2] and 0.21 mole of the diene (containing not more than 5% of impurities by GLC) was cooled to −5° C and stirred for 4 hr, the pH adjusted to 5.8–6.8 by treatment in the cold with 50% KOH, extracted with ether, and the ether washings discarded. Water was distilled off in vacuo on a bath at 40–50° C to constant weight, and the residue extracted with chloroform. The solvent was distilled off, and the viscous oil was crystallized by treatment with a small amount of acetone. The reaction product was recrystallized from ethyl acetate–isopropanol (2 : 1) (see table).

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18 April 1968

Kirov Academy of Military Medicine, Leningrad