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SYNTHESIS OF 1-VINYL-1-(α-AMINOALKYL)CYCLANES FROM IMINES AND 1,1-POLYMETHYLENALLENES THROUGH ALLYLBORANES

Yu. N. Bubnov, V. I. Zheludeva,
T. Yu. Rudashevskaya, and T. S. Kuznetsova

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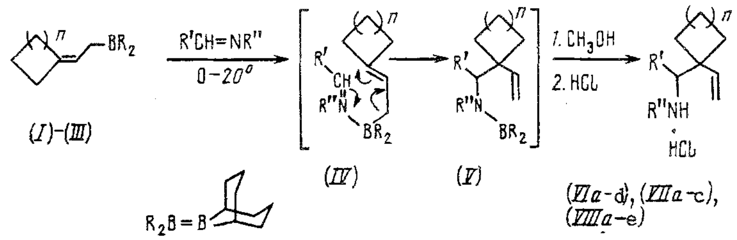
β,γ-Unsaturated (allylic) derivatives of boron react with carbonyl compounds, nitriles, and imines by 1,2-addition of the boron—allyl fragments to the multiple bond [1, 2]. Convenient methods for the synthesis of butenylamines [3-5], 4-amino-1,6-heptadienes [7, 8], amino acids [4], and other nitrogen compounds [6, 9] have been developed using the allylborylation of nitriles and imines. The reaction usually proceeds regio- and stereoselectively due to the rigid orientation of the substituents in the six-centered chairlike transition state [2-5].

In a continuation of a study of new boroallylic systems [2], we investigated the reactions of 9-(3,3-trimethylenallyl)- (I) [10], 9-(3,3-tetramethylenallyl)- (II), and 9-(3,3-pentamethylenallyl)-9-borabicyclo[3.3.1]nonanes (III) [11] with aldimines and a general method of the preparation of gem-substituted unsubstituted cyclobutylamines (IX), cyclopentylamines (X), and cyclohexylamines (XI) was developed using these reactions.

The reactions of boranes (I)-(III) with imines R'CH=NR" proceeds at 0-20°C and lead to the corresponding aminoboranes (V), which give hydrochlorides (VIa)-(VId), (VIIa)-(VIIc), (VIIIa), and (VIIIc-e) in 60-93% yield (Table 1).



(I)-(III)

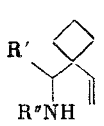
(IV)

(V)

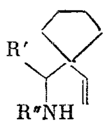
(VIa-d), (VIIa-c), (VIIIa-e)

$R' = Ph$, $R'' = Me$ (a); $R' = Ph$, $R'' = n\text{-}C_6H_{13}$ (b); $R' = Me_2CH$, $R'' = Me$ (c); $R' = Me_2CH{-}CH_2$, $R'' = Me$ (d); $R' = \alpha$-thienyl, $R'' = Me$ (e).
$n = 1$ (I), (VI); $n = 2$ (II), (VII); $n = 3$ (III), (VIII).

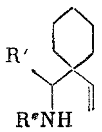
The addition of boranes (I)-(III) to imines is achieved with allylic rearrangement, apparently through transition state (V). These reactions proceed smoothly and are not complicated by side reactions as often observed in the alkylation of imines by organomagnesium and organolithium compounds [4]. Furthermore, the allylborylation of these imines may be carried out without solvent or in any inert solvent such as hydrocarbons, chloroform, CCl_4, ether, and THF, which is important when using solid imines. Hydrochlorides (VI)-(VIII) are converted by the action of NaOH to the corresponding amines (IX)-(XI) (Table 1).



(IX)



(X)



(XI)

The combination of these reactions along with hydroborylation is a convenient preparative method for obtaining unsaturated amines (IX)-(XI) from 1,1-polymethylenallenes and Schiff

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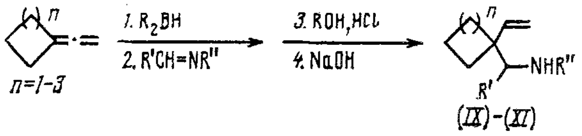
TABLE 1. Properties of Amines (IX)-(XI) and Their Hydrochlorides (VI)-(VIII)

Amine	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	Found/Calculated, %		Hydro-chloride	Yield, %	Mp, °C	Found/Calculated, %		
				C	H				C	H	Cl
(IXa)	71	85–87(1)	1,5342	83,70/83,53	9,55/9,51	(VIa)	81	257–259	70,84/70,71	8,48/8,48	15,15/14,92
(IXb)	79	122–123(1)	1,5092	84,27/84,07	10,88/10,77	(VIb)	83	164–165	74,23/74,11	10,10/9,81	11,63/11,52
(IXc)	67	40–41(1)	1,4672	78,97/78,98	12,70/12,65	(VIc)	86	199–201	65,07/64,83	11,04/10,88	17,44/17,42
(IXd)	79	44–45(1)	1,4651	79,66/79,49	12,58/12,78	(VId)	84	204–206	65,79/66,17	11,06/11,11	16,46/16,29
(Xa)	80	102–103(1)	1,5339	84,00/83,67	9,89/9,83	(VIIa)	88	273–275	71,49/71,54	9,00/8,81	13,75/14,09
(Xb)	70	127–128(1)	1,5125	84,32/84.15	11,00/10,95	(VIIb)	71	136–137	74.69/74,61	10.19/10,02	11,41/11,02
(Xc)	67	53–54(1)	1,4718	79,13/79,49	12,89/12,73	(VIIc)	76	174–175	66,05/66,17	11,29/11,11	16,62/16,29
(XIa)	70	112–113(1)	1,5396	83,81/83,79	10,22/10,11	(VIIIa)	70	272–273	72,40/72,32	9,13/9,04	13,68/13,37
(XIc)	70	69–70(1)	1,4818	79,91/79,93	12,87/12,90	(VIIIc)	93	199–200	67,15/67,35	11,36/11,30	15,87/15,31
(XId)	63	85–87(1)	1,4774	80,45/80,31	12,93/13,00	(VIIId)	60	161–162	68,49/68,39	11,45/11,48	14,23/14,44
(XIe)	66	117–118(1)	1,5437	71,62/71,49	9,14/8,94	(VIIIe)	71	236–237	61,89/61,88	8,19/8,10	13,08/13,08

bases.



$n = 1$ (IX) 2 (X), 3 (XI).

The structures of hydrochlorides (VI)-(VIII) and amines (IX)-(XI) were supported by elemental analysis and spectral methods. The IR spectra of the hydrochlorides in $CHCl_3$ and the amines show bands for the terminal double bond at 910-920, 1635-1645, and 3080-3095 cm^{-1}. The broad band for the ammonium group at 2700-2800 cm^{-1} in (VI)-(VIII) is superimposed on the CH_2 and CH_3 stretching bands. The NH group band in (IX)-(XI) appears at 3330-3385 cm^{-1}. The PMR spectra of the amines and their hydrochlorides show signals at 5.5-6.3 (CH=C), 4.9-5.6 ppm (CH=C). The signals for the protons of the $[R_2NH_2]^+$ group in the spectra of the hydrochlorides are found at 8.4-9.9 ppm.

EXPERIMENTAL

All the operations with organoboron compounds were carried out in a dry argon atmosphere. The PMR spectra were measured on a Bruker WM-250 spectrometer. The IR spectra were taken on a UR-20 spectrometer.

1-Vinyl-1-(α-hexylaminobenzyl)cyclobutane Hydrochloride (VIb). A samples of 1.4 g borane (I) was added to a three-necked flask equipped with a magnetic stirrer, thermometer, and dropping funnel and then, 1.12 g N-hexylbenzaldimine was added at 10°C. The mixture was stirred for 2 h at 20°C and 15 ml pentane was added. Then 0.5 ml methanol and 3.5 ml 2.45 M ethereal HCl were added at 0°C. The crystalline precipitate was filtered off and washed with ether to give 1.52 g (83%) hydrochloride (VIb), mp 164-165°C.

Analogous procedures gave hydrochlorides (VIa)-(VId), (VIIa)-(VIIc), (VIIIa), and (VIIIc)-(VIIIe).

1-Vinyl(α-hexylaminobenzyl)cyclobutane (IXb). A sample of 28 ml 0.1 M NaOH was added to a solution of 0.87 g (VIb) in 15 ml water and the mixture was stirred for 0.5 h. The organic layer was separated and the aqueous layer was extracted with three 20-ml portions of ether. The combined organic layer and ethereal extracts were dried over $MgSO_4$. Removal of the solvent and distillation gave 0.61 g (79%) amine, bp 122-123°C (1 mm).

Analogous procedures gave amines (IX), (X), and (XI) (see Table 1).

CONCLUSIONS

A method has been developed for the preparation of gem-disubstituted butenylamine derivatives of cyclobutane, cyclopentane, and cyclohexane by the allylborylation of Schiff bases (imines).

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