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REACTION OF DIBUTYL PHENYLBORATE WITH HEXAMETHYLDISILAZANE AND HEXAMETHYLCYCLOTRISILAZANE

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UDC 542.91:547.558.4+546.273-325:547.1'128

A study was carried out on the reaction of dibutyl phenylborate with hexamethyldisilazane and hexamethylcyclotrisilazane in the presence of a catalyst, which leads to B-triphenylborazine and various butoxysilazanes. The formation of a mixed B,N,O heterocyclic compound is also observed in the reaction with hexamethyldisilazane.

The synthesis of B,N heterocyclic compounds continues to attract attention [1]. Only liquid products have been obtained as a result of the reaction of tributoxyboron with octamethylcyclotetrasilazane and hexamethylcyclotrisilazane (HMCS) [2]. These products are a set of linear silazanes with terminal butoxy groups and do not contain boron.

We have studied the reaction of dibutyl phenylborate (DBPB) with hexamethyldisilazane (HMSN) and HMCS in the presence of 0.3% sulfuric acid.

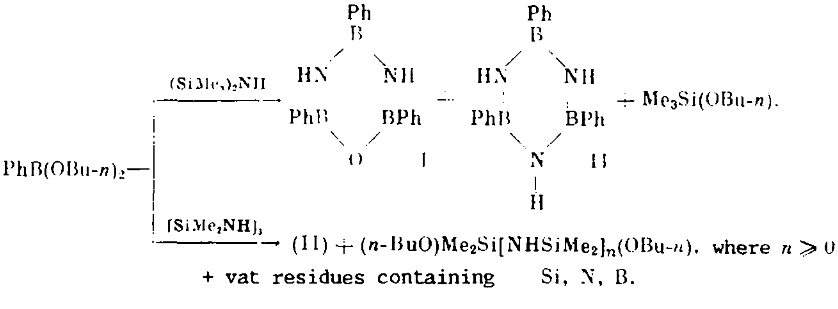

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TABLE 1. Reaction of Silazanes with Dibutyl Phenylborate

Silazane, mole	$PhB(OBu\text{-}n)_2$, mole	Time, h	Isolated, %			
			(I)	(II)	starting silazane	starting PhB(OBu-n)
HMSN, 0,1	0,05	4.5	30	–	50	50
HMSN, 0,025	0,025	11,0	27	–	30	46
HMSN, 0,1	0,05	15,0	48% mix. of (I) and (II)		30	40
HMCS, 0.05	0,05	11,0	–	36	30	32
HMCS, 0,04	0,03	11,0	–	24	–	–
HMCS, 0,054	0,08	7,0	–	24	–	–

TABLE 2. Boron Heterocycles

Compound	Mp, °C	Found/Calculated, %				IR spectrum, ν, cm^{-1}
		C	H	N	B	
(I)	173–174	69,37/69,74	5,97/5,85	9,62/9,04	9,90/10,46	3448 (N–H) 1350 (B–O)
(II)	182–183	70,88/70,02	6,70/5,87	13,22/13,61	10,09/10,50	3440 (N–H) 1468 (B–N)

The reaction conditions and yields of the final products are given in Table 1. Linear silazanes with terminal butoxy groups were isolated in addition to the starting reagents from the mixture of liquid products after distillation. The structure of these linear silazanes was in accord with that given by Andrianov et al. [2]. Products (I) and (II) were isolated from the solid products by recrystallization. The structures of these compounds were supported by IR spectroscopy and elemental analysis (Table 2). These data for (II) are in accord with literature values [3].

Thus, the reaction proceeds with cleavage of the B–O and Si–N bonds with formation of a B–N bond and subsequent ring closure. The reaction of HMCS and DBPB gives only heterocycle (II), which corresponds to our results on the synthesis of B-triphenylborazine from phenylboric anhydride and HMCS [4]. The reaction of DBPB with HMCS gives the predominant formation of mixed heterocycle. The yield of product (I) depends on the reaction time and reagent ratio. The reaction conditions do not exclude the possibility of the condensation of DBPB with loss of dibutyl ether and formation of a B–O–B fragment, which is then included in heterocycle (I).

EXPERIMENTAL

The gas-liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph on 2000 × 4-mm columns packed with 5% SE-30 on Inerton AW-HMDS (0.2-0.25 mm). The nitrogen gas carrier flow rate was 30 ml/min with a katharometer detector. The IR spectra were taken on a UR-20 spectrometer.

General Procedure for the Reaction of DBPB with HMSN and HMCS. A sample of 0.3% concentrated sulfuric acid was added to a mixture of DPBP with the silazane and heated at reflux with continuous argon flushing. At the end of the heating, the crystalline portion was filtered off and recrystallized from hexane. The liquid portion was distilled off and subjected to chromatography.

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STEREOISOMERISM OF β-POLYFLUOROALKYL-α,β-ENONES

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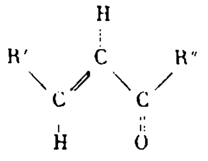
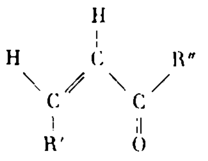
β-Polyfluoroalkyl-α,β-enones formed in the E,Z form are converted by the action of atmospheric oxygen into a 93:7 mixture of E,Z and Z,E isomers in the dark and 60:40 mixture of these isomers in the light. The Z isomer of 1-phenyl-4,4,4-trifluoro-2-buten-1-one was isolated preparatively for the first time and its E conformation relative to the C—C bond was established. The Z,E isomer spontaneously transforms into the indicated equilibrium mixtures.

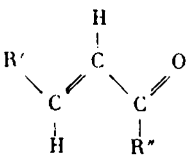
Theoretically, α,β-enones may exist as four spatial isomers:



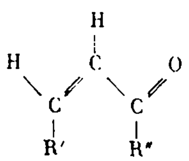
E, Z



Z, Z



E, E

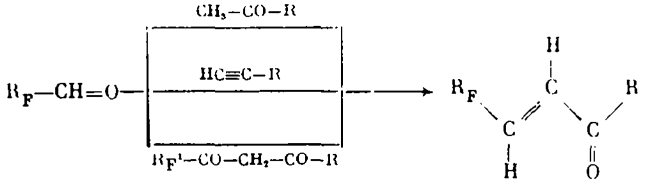


Z, E

Nonfluorinated α,β-enones are characterized by an equilibrium mixture of Z and E isomers with predominance of the E isomer [1]. The barrier to rotation about the double bond $\Delta G^{\neq}$ = 9-19 kcal/mole [2]. The fraction of the Z isomer increases in the presence of acids [3] and upon the introduction of electron-withdrawing β-substituents [1].

Ogoshi et al. [4] reported the separation of 1,1,1-trifluoro-2-penten-4-one as a 95:5 equilibrium mixture of E and Z isomers relative to the double bond without considering s-Z,s-E isomerism.

In previous work [5-7], we used IR, Raman, and PMR spectroscopy to establish that β-polyfluoroalkyl-α,β-enones (Ia)-(If) are formed exclusively as the E,Z form independently of the method of preparation:



(Ia-e)

$R_F = CF_3$(a), C_4F_9 (b-d), C_6F_{13}(e, f); R = Me(b), *t*-Bu(c, f), Ph(a, d, e).

In the present work, we studied the isomerization of β-polyfluoroalkyl-α,β-enones (Ia)-(If) and established that the E,Z form does not undergo any change upon storage in the dark with access to air for one year as indicated by thin-layer chromatography and IR spectroscopy. On the other hand, in the light or upon storage in the dark with access to air, some of these β-polyfluoroalkyl-α,β-enones (Ia)-(If) form mixtures of E and Z isomers. The isomerization upon UV irradiation requires 24-48 h (s-E,s-Z isomerism is discussed below).

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