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Homolytic Reactions of *N*-Bromohexamethyldisilazane with Trialkyl(phenylalkoxy) Derivatives of Silicon and Tin

V. I. Rakhlin, T. A. Podgorbunskaya, and M. G. Voronkov

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: vir@irioch.irk.ru

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Abstract—The main product of the photoinduced reaction of N-bromohexamethyldisilazane with trialkyl-(benzyloxy)derivatives of silicon and tin $R_3MO(CH_2)_nPh$ (R = Me, Et; M = Si, Sn; n = 1) is *N,N*-dibenzylidene-*C*-phenylmethanediamine (hydrobenzamide). For M = Si, with increase of the length of the methylene chain between the oxygen atom and the phenyl group (n = 2, 3), the similar reaction affords the product of bromination of the benzylic carbon atom $R_3MO(CH_2)_{n-1}CHBrPh$. For M = Sn, the reaction results in the formation of 2-phenyloxacycloalkanes $PhCHO(CH_2)_{n-1}$.

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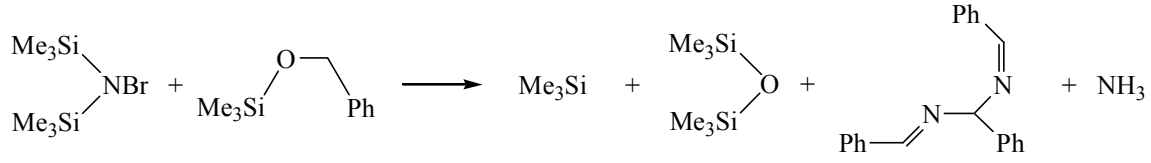
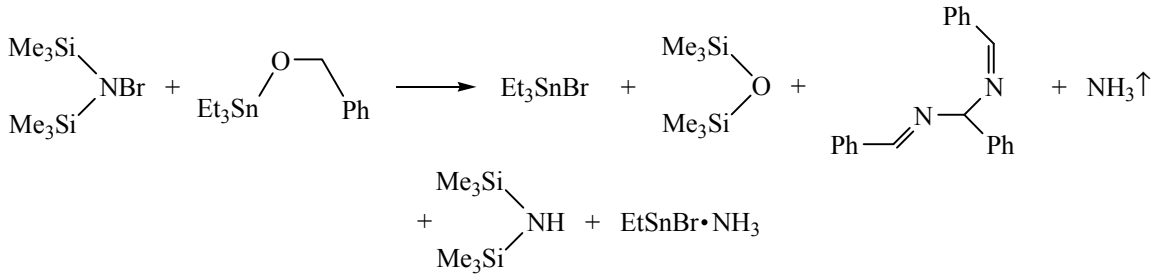
N-Bromohexamethyldisilazane is a promising brominating agent for fine organic synthesis. Its main advantage over other widely used brominating agents (elemental bromine, *N*-bromo-succinimide, etc.) is that in the reaction of homolytic bromination with *N*-bromohexamethyl-disilazane elimination of the hydrogen atom from the substrate proceeds with participation of the N-centered hexamethyldisilazanyl radical $(Me_3Si)_2N^{\cdot}$ [1] rather than $Br^{\cdot}$, as usual, thus changing the selectivity of the reaction. However, the reactivity of *N*-bromohexamethyldisilazane is poorly studied [2]. There are practically no data on its interaction with organoelement compounds although in some cases it was shown to proceed with the formation of unexpected products. Thus, we have earlier reported that the reaction of *N*-bromohexamethyl-disilazane with triorganylsilanes $R^1R^2R^3SiH$ affords the corresponding unsymmetric silazanes $R^1R^2R^3SiNHSiMe_3$ in practically quantitative yield [3]. The present work is devoted to investigation of the course of the reaction of *N*-bromohexamethyl-disilazane with (phenylalkoxy) derivatives of silicon and tin of the general formula $R_3MO(CH_2)_nPh$, where R = Me, Et; M = Si, Sn; n = 1–3.

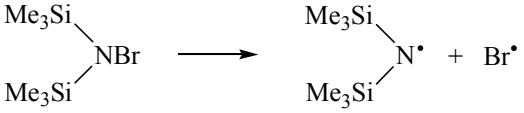
First, we investigated the reaction of *N*-bromo-hexamethyl-disilazane with trimethyl(benzyloxy)-silane. After 4 h of the UV-irradiation of the equimolar mixture of the reagents placed into evacuated sealed ampoule, the formation of a precipitate was observed, and after opening the ampoule ammonia was evolved. The liquid fraction consists of the mixture of trimethylbromosilane and hexamethyl–disiloxane, whereas the solid product was assigned the structure of *N,N*-dibenzylidene-*C*-phenylmethanediamine (hydro-benzamide) judged from the data of NMR spec-troscopy.



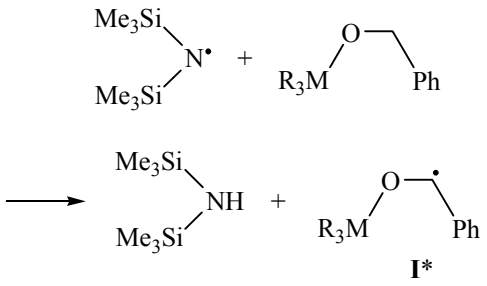
The products of the similar reaction of *N*-bromo-hexamethyldisilazane with triethylbenzyloxystannane turned out to be hexamethyldisiloxane, hexamethyl-disilazane, hydrobenzamide, ammonia, triethylbromo-stannane, and the complex of triethylbromo-stannane with ammonia.



Earlier, we have shown that hexamethyldisilazane reacts with benzaldehyde to give hydrobenzamide [4], therefore, it is reasonable to assume the formation of benzaldehyde in the above reactions as an intermediate. The following mechanism can be suggested. Upon the UV irradiation, *N*-bromohexamethyl-disilazane is decomposed to the hexamethyldisilazanyl radical and bromine radical:

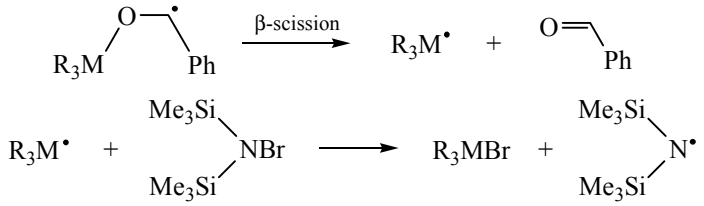


Then, the hexamethyldisilazanyl radical formed abstracts the benzylic hydrogen atom to give radical (**I***):

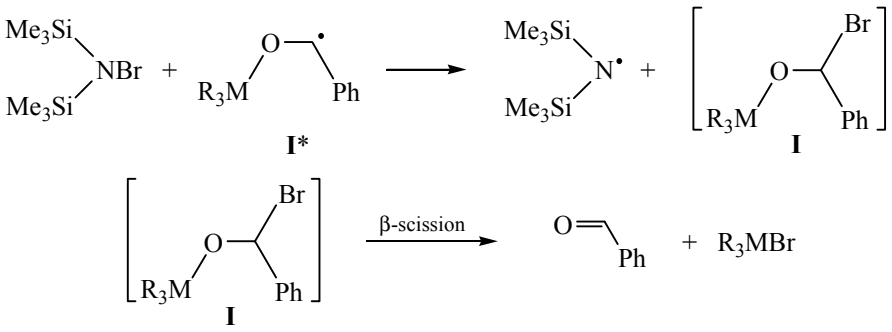


R = Et, M = Sn; R = Me, M= Si.

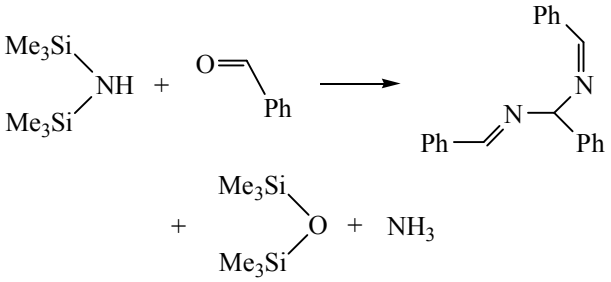
The latter can undergo β-scission leading to benzaldehyde and the element-centered radical $R_3M^{\cdot}$, which can further abstract the bromine atom from *N*-bromohexamethyldisilazane with the formation of the corresponding bromide:



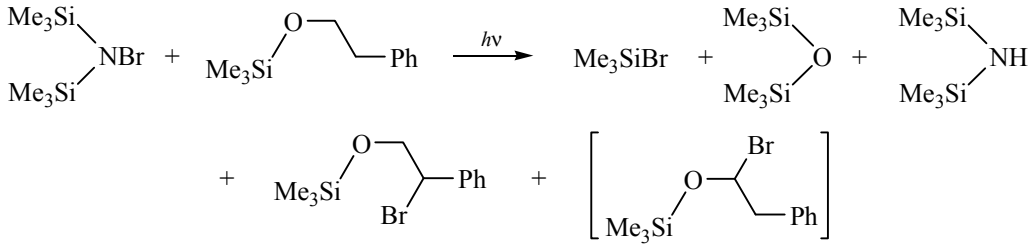
An alternative possibility of the formation of benzaldehyde is the abstraction by radical (**I***) of the bromine atom from *N*-bromohexamethyldisilazane leading to the unstable intermediate product $R_3MOCHBrPh$ (**I**), capable of β-scission:



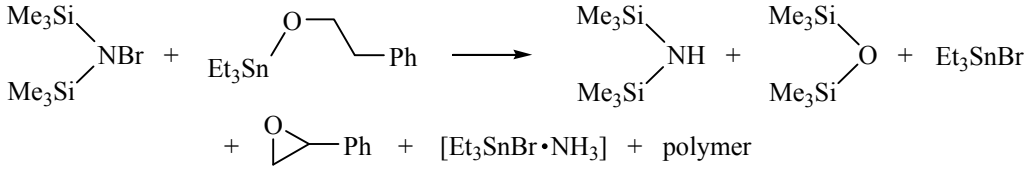
The formed benzaldehyde, in turn, readily reacts with hexamethyldisilazane by the scheme:



Next, we have studied the photoinduced reaction of (phenethyloxy)derivatives of silicon and tin with *N*-bromohexamethyldisilazane. GC analysis of the reaction mixture obtained after the UV irradiation of the equimolar mixture of *N*-bromohexamethyldisilazane with trimethyl(phenethyloxy)silane has shown the presence of trimethylbromosilane, hexamethyldisiloxane, hexamethyldisilazane, as well as two high-boiling products. One of them was the product of the reaction of homolytic substitution of hydrogen atom in the benzylic position of the substrate by the bromine atom, $Me_3SiOCH_2CH(Br)Ph$, its structure was proved by NMR spectroscopy. The second product decomposed during isolation and, apparently, was the product of substitution of hydrogen atom at the α-carbon atom with respect to the oxygen atom, $Me_3SiOCH{\cdot}(Br)CH_2Ph$.

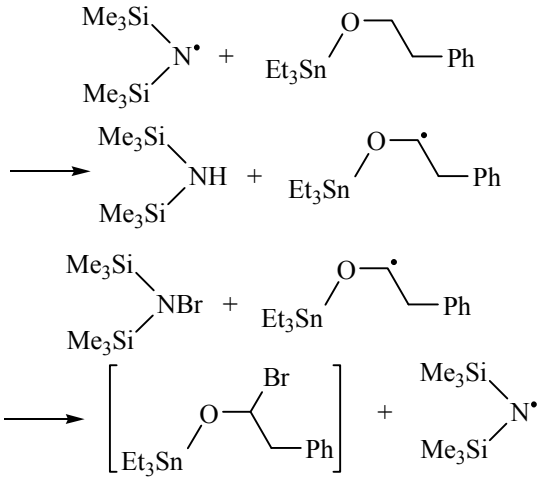


The reaction with triethyl(phenethyloxy)stannane led to the formation of hexamethyldisilazane, small amount of hexamethyldisiloxane, triethylbromostannane, and 2-phenyloxirane. A small amount of crystals consisting of a mixture of complex $[Et_3SnBr{\cdot}NH_3]$ and a polymeric crystalline product was also formed:

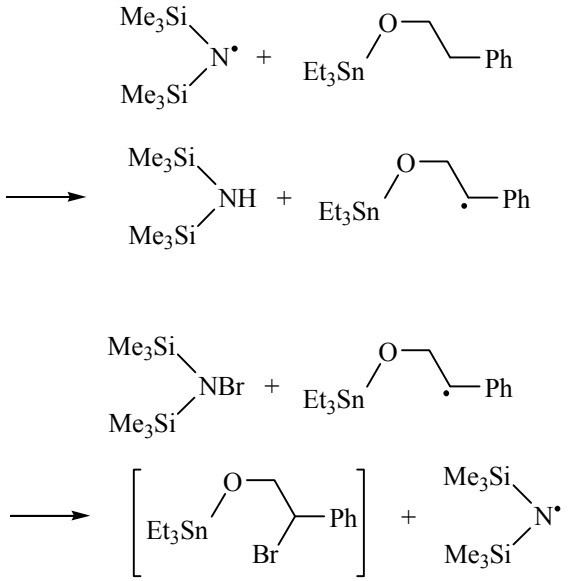


The mechanism of the reaction can be represented by the following scheme. The bromination may proceed in two directions:

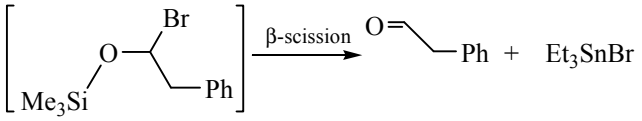
(a) First direction:



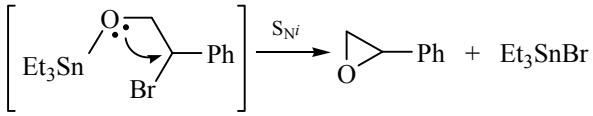
(b) Second direction:



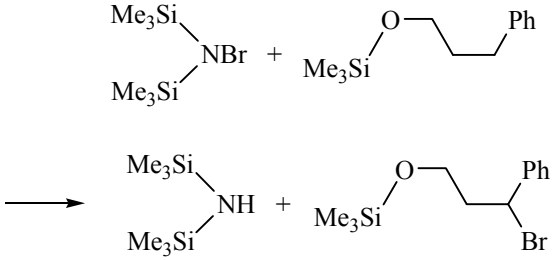
The product of bromination formed in the first case suffers β-scission leading to phenylacetic aldehyde and triethylbromostannane:



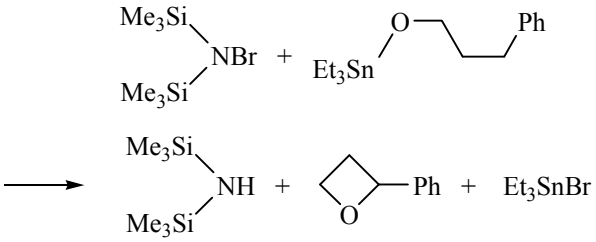
As to the crystalline product, it is reasonable to assume that it stems from the reaction of hexamethyldisilazane with phenylacetic aldehyde $PhCH_2 \cdot C(O)H$. In the product of bromination formed by the second direction the oxygen atom can enter the reaction of intramolecular nucleophilic substitution leading to 2-phenyloxirane and triethylbromostannane. The reaction is facilitated by enhanced nucleophilicity of the oxygen atom attached to the triethylstannyl group:



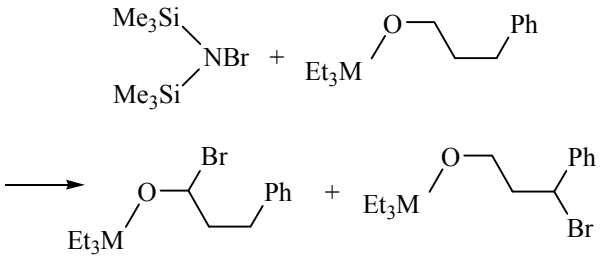
The main product of the photoinduced reaction of trimethyl(3-phenylpropoxy)silane with *N*-bromohexamethyldisilazane is trimethyl(3-bromo-3-phenylpropoxy)silane:



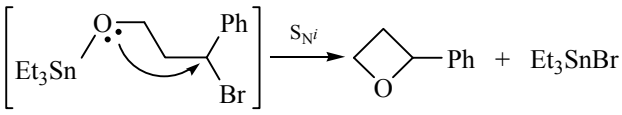
The similar reaction of triethyl(3-phenylpropoxy)-stannane results in 2-phenyloxetane**,** triethylbromostannane and hexamethyldisilazane with small amount of hexamethyldisiloxane.



The structure of the products of these reactions is indicative of similarity of their mechanisms and the mechanisms of bromination of trialkyl(phenethyloxy) silanes and -stannanes discussed above. Apparently, the reaction also proceeds with the initial formation of the products of bromination at the α-carbon atom with respect to the oxygen atom and the at the benzylic carbon atom of the substrate.



For M = Si, the former product suffers b-scission upon rectification and the product isolated in 35% yield is trimethyl(3-bromo-3-phenylpropoxy)silane. For M = Sn, the product of bromination at the benzylic carbon atom undergoes the reaction of intramolecular nucleophilic substitution leading to 2-phenyloxetane in 88% yield.



Interestingly, in the reaction with triethyl(3-phenylpropoxy)stannane the crystalline product was practically absent but in the ^{1}H NMR spectrum of the reaction mixture we observed the signals characteristic of phenylpropionic aldehyde, which was found in trace amounts. This fact, as well as a high yield of 2-phenyloxetane allows to conclude that the bromination proceeds mainly at the benzylic carbon atom.

EXPERIMENTAL

^{1}H, ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with working frequency of 400.1 (^{1}H), 100.61 MHz (^{13}C) in $CDCl_3$, internal standard TMS. GC analysis was performed on a Tsvet-500 chromatograph, detector is catharometer, glass columns 3 m×4 mm, sorbent is Inerton-super 0.125–0.150 mm with 10% PSM-1000, gas-carrier–helium. For the UV irradiation of the reaction mixtures a DRT-400 lamp was used.

N-Bromohexamethyldisilazane was prepared by the reaction of *N*-bromosuccinimide with hexamethyldisilazane [5]. Trimethyl(aryloxy)silanes were synthesized by the reaction of the corresponding arylalkanoles with hexamethyldisilazane in the presence of catalytic amount of $(NH_4)_2SO_4$ [6]. Triethyl(arylalkoxy)stannanes were obtained by reetherification of

triethylmethoxystannane by the appropriate arylalkanoles [7].

Reaction of trimethyl(benzyloxy)silane with *N*-bromohexamethyldisilazane. The equimolar mixture of 12.6 g (0.07 mol) of trimethyl(benzyloxy)silane and 16.8 g (0.07 mol) of *N*-bromohexamethyldisilazane was charged into a dry reaction tube, degassed by the freezing/defreezing method, sealed and irradiated by the UV light for 4 h. After opening the tube, 0.6 g (48%) of ammonia evolved from the reaction mixture was trapped. The formed crystalline product was filtered from the liquid phase. After distillation of the latter, 5.9 g (72%) of hexamethyldisiloxane with bp 100ºC, n_D^{20} 1.3774, and 6.7 g (62%) of trimethylbromosilane was obtained. The precipitate purified by reprecipitation from chloroform into hexane contained 8.2 g (39%) of hydrobenzamide; ^{1}H NMR (δ, ppm): 8.57 s (1H, –CH=N–); 7.86–7.79, m (5H, C_6H_5); 7.4–7.33 m (10H, C_6H_5–C=N–); 5.94 s (1H, –CHN_2-).

Reaction of triethyl(benzyloxy)stannane with *N*-bromohexamethyldisilazane. The equimolar mixture of 21.9 g (0.07 mol) of triethyl(benzyloxy)stannane and 16.8 g (0.07 mol) of *N*-bromohexamethyldisilazane was charged into a dry reaction tube, degassed by the freezing/defreezing method, sealed and irradiated by the UV light for 4 h. The formed crystalline product was filtered from the liquid phase. After distillation of the latter, 2.8 g (34%) of hexamethyl-isiloxane, 4.7 g (42%) of hexamethyldisilazane with bp 35ºC (35 mm Hg), n_D^{20} 1.4080 and 12.5 g (62%) of triethylbromostannane with bp 97ºC (13 mm Hg), n_D^{20} 1.5240 was obtained. The precipitate was separated and purified by reprecipitation from chloroform into hexane; it contained 5.3 g (25%) of hydrobenzamide and 3.3 g (16%) of complex [$Et_3SnBr{\cdot}NH_3$].

Reaction of trimethyl(phenethyloxy)silane with *N*-bromohexamethyldisilazane. The equimolar mixture of 13.6 g (0.07 mol) of trimethyl(phenethyloxy)silane and 16.8 g (0.07 mol) of *N*-bromohexamethyldisilazane was charged into a dry reaction tube, degassed by the freezing/defreezing method, sealed and irradiated by the UV light for 6 h. After distillation at atmospheric pressure 2.6 g (31%) of hexamethyldisiloxane, 8.2 g (72%) of hexamethyldisilazane, and 1.1 g (10%) of trimethylbromosilane was obtained. Vacuum distillation gave 6.9 g (36%) of trimethyl(2-bromo-2-phenylethoxy)silane with bp 167ºC (3 mm Hg); ^{1}H NMR (δ, ppm): 0.1 s (9H, Me_3Si); 4.15–4.02 t (2H, –CH_2–); 4.99–4.95 m (1H, –CHBr–); 7.57–7.23 m (5H, C_6H_5).

Reaction of triethyl(phenethyloxy)stannane with *N*-bromohexamethyldisilazane. The equimolar mixture of 22.9 g (0.07 mol) of triethyl(phenethyloxy)-stannane and 16.8 g (0.07 mol) of *N*-bromohexamethyldisilazane was charged into a dry reaction tube, degassed by the freezing/defreezing method, sealed and irradiated by the UV light for 4 h. The formed crystalline product was filtered from the liquid phase. After distillation of the latter, 4.5 g (54%) of hexamethyldisiloxane, 5.5 g (49%) of hexamethyldisilazane, 10.0 g (50%) of triethylbromostannane, and 7.5 g (89%) of 2-phenyloxirane with bp 74ºC (12 mm Hg), n_D^{20} 1.5632 was obtained. ^{1}H NMR of 2-phenyloxirane (δ, ppm): 2.8–2.71 m (2H, –H_2CO–); 3.86–3.04 m (1H, –CH–); 7.38-7.18 m (5H, C_6H_5). The precipitate was separated and purified by reprecipitation from chloroform into hexane; it contained 6.4 g (30%) of complex [$Et_3SnBr{\cdot}NH_3$] and a polymeric product.

Reaction of trimethyl(3-phenylpropoxy)silane with *N*-bromohexamethyldisilazane. The equimolar mixture of 14.6 g (0.07 mol) of trimethyl(3-phenylpropoxy)silane and 16.8 g (0.07 mol) of *N*-bromohexamethyldisilazane was charged into a dry reaction tube, degassed by the freezing/defreezing method, sealed and irradiated by the UV light for 4 h. After distillation at atmospheric pressure 3.8 g (46%) of hexamethyldisiloxane, 9.2 g (82%) of hexamethyldisilazane, and 0.1 g (0.5%) of trimethylbromosilane was obtained. Vacuum distillation gave 7.1 g (35%) of trimethyl(3-bromo-2-phenylpropoxy)silane with bp 123ºC (2 mm Hg), n_D^{22} = 1.5062; ^{1}H NMR (δ, ppm): 0.17 s (9H, Me_3Si); 2.44–2.27 m (2H, –CH_2–); 2.52–2.48 m (2H, CH_2Ph); 5.74–5.71 m (1H, –CHBr); 7.58–7.13 m (5H, C_6H_5).

Reaction of triethyl(3-phenylpropoxy)stannane with *N*-bromohexamethyldisilazane. The equimolar mixture of 23.9 g (0.07 mol) of triethyl(3-phenylpropoxy)stannane and 16.8 g (0.07 mol) of *N*-bromohexamethyldisilazane was charged into a dry reaction tube, degassed by the freezing/defreezing method, sealed and irradiated by the UV light for 8 h. After distillation 3.2 g (38%) of hexamethyldisiloxane, 6.9 g (61%) of hexamethyldisilazane, and 9.3 g (47%) of trimethylbromostannane with bp 97ºC (13 mm Hg), n_D^{20} 1.5240 was obtained. Vacuum distillation gave 8.2 g (88%) of 2-phenyloxetane with bp 91ºC (9 mm Hg), n_D^{20} 1.5456; ^{1}H NMR (δ, ppm): 3.03–2.53 m (2H, –CH_2–); 4.83–4.59 m (2H, –CH_2O); 5.82–5.77 m (1H, –CH–); 7.29–7.12 m (5H, C_6H_5).

ACKNOWLEDGMENTS

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