(7), $[M - C_2H_5]^+$ 103 (25), $[M - H_2S]^{+\cdot}$ 98 (13), $[M - C_2H_5CHO]^+$ 74 (100), 73 (25), 70 (23), 59 (12), 47 (20), 45 (35), 41 (100), 39 (33).

Dibutyl Disulfide (VI). Mass spectrum, m/z (I_{rel}): $[M]^{+\cdot}$ 178 (25), $[M - Bu]^+$ 121 (28), $[Bu]^+$ 57 (100), $[C_3H_5]^+$ 41 (55).

Butyl Methyl Sulfide (VII). Mass spectrum, m/z (I_{rel}): $[M]^{+\cdot}$ 104 (60), $[M - Me]^+$ 89 (5), $[M - Et]^+$ 75 (17), $[CH_3SCH_2]^+$ 61 (100), 56 (80), $[SCH_3]^+$ 47 (25), $[C_3H_5]^+$ 41 (25).

Triphenylmethane (IX). Mass spectrum, m/z (I_{rel}): $[M]^{+\cdot}$ 244 (100), $[M - H]^+$ 243 (25), $[M - Ph]^+$ 167 (85), $[M - PhH]^{+\cdot}$ 166 (50), $[M - PhCH_2]^+$ 153 (20).

1,1,1-Triphenylethane (X). Mass spectrum, m/z (I_{rel}): $[M]^{+\cdot}$ 258 (10), $[M - Me]^+$ 243 (100), $[M - PhCH_2]^+$ 167 (52), 77 (15).

LITERATURE CITED

1. A. N. Nesmeyanov, Methods in Heteroorganic Chemistry. Magnesium [in Russian], Izd. Akad. Nauk SSSR, Moscow (1963), p. 390.
2. H. Yamatama, T. Matsuama, and T. Hanafusa, J. Am. Chem. Soc., 111, No. 13, 4912 (1987).
3. Yu. N. Polivin, R. A. Karakhanov, and V. N. Postnov, Usp. Khim., 59, No. 3, 401 (1990).
4. F. Babudri, S. Florio, and G. Ingusto, Synthesis, No. 5, 522 (1985).
5. M. Ohno, K. Shimizu, and R. Ishizari, J. Org. Chem., 53, No. 4, 729 (1988).
6. Yu. N. Polivin, C_α—C_β Dissociation of Ferrocene-Containing β-Dicarbonyl Compounds, Author's Abstract of Chemical Sciences Candidate's Dissertation, Moscow (1984).
7. S. Brown, J. Am. Chem. Soc., 74, 258 (1952).
8. N. Kaufman and A. Adams, Am. Chem. J, 45, 1747 (1911).
9. E. Gilman, S. Smith, and R. Parker, Am. Chem. J., 46, 859 (1912).

HYDROSILYLATION AND HYDROGERMYLATION OF 3-OXO-1,2-BENZISOTHIAZOLINE-2-(2-PROPYNYL)-1,1-DIOXIDE

G. S. Lyashchenko, A. S. Medvedeva,
L. P. Safronova, O. B. Bannikova,
and M. G. Voronkov

UDC 542.91:547.1'128:547.246:547.77

The addition of triethylsilane and triethylgermane to N-propargylsaccharin in the presence of the Speier catalyst gives the gem adduct with trans configuration. This pathway accounts for 75-80% of the reaction.

In previous work [1-4], one of us had shown that the hydrosilylation and hydrogermylation of 3-phenoxy- and 3-phenylthio-1-propynes in the presence of the Speier catalyst, which is a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol, proceeds without regiospecificity or stereospecificity.

In a continuation of a study of the effect of the heteroatom in the β-position relative to the triple bond on the direction of hydrosilylation and hydrogermylation reactions, we studied the addition of triethylsilane (I) and triethylgermane (II) to a nitrogen analog of aromatic heteroatomic propyne derivatives, namely, 3-oxo-1,2-benz-isothiazoline-2-(2'--propynyl) 1,1-dioxide (N-propargylsaccharin) (III) in the presence of the Speier catalyst.

The synthesis of new saccharin derivatives also holds interest in the search for new biologically active compounds since some N-substituted saccharins are known to be active fungicides [5], while nitrogen-containing organic compounds, in which the silicon and nitrogen atoms are separated by three carbon atoms have high antimicrobial activity [6].

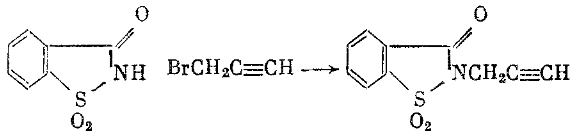
Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2889-2891, December, 1991. Original article submitted February 19, 1991.

0568-5230/91/4012-2520$12.50

TABLE 1. PMR Spectral Parameters of N-Propargylsaccharin and Its Adducts with Et_3GeH and Et_3SiH (δ, ppm, J, Hz)

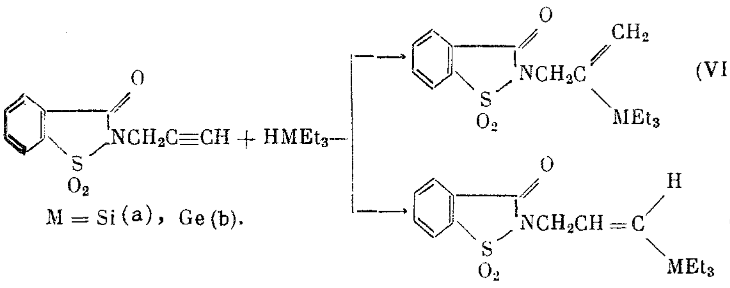
Compound	=CH (nonterminal)	=CH (terminal)	C_6H_4	Et_3	CH_2	^2J	^3J	^4J
(III)		2,37t (–C≡H),	7,97m		4,53 d			2.68
(VIa)		5,47 br.d 5,81 br.d	7,88 m	0,95m	4,38br.s	1,2		
(VIb)		5,39 br.d 5,83 br.d	7,90m	1,03m	4,46br.s	0,8		
(VIIa) (trans)	6,06 m	6,05m	7,88 m	0,95m	4,38 m		4,0	
(VIIb) (trans)	6,12t	6,17 s	7,90 m	1,03m	4,40d		4,0	

Sodium saccharinate is usually employed with the corresponding organyl halides in order to obtained N-substituted saccharin derivatives [7, 8]. In contrast, previously unreported N-propargylsaccharin (III) was obtained in 70% yield by the reaction of saccharin (IV) with propargyl bromide (V) in DMF in the presence of K_2CO_3 and catalytic amounts of KI.



(III).

The addition of (I) to (III) in the presence of Speier catalyst in THF at 70°C proceeds with the formation of 3-oxo-1,2-benzothiazoline-2-(2'-triethylsilyl-2'-propenyl) 1,1-dioxide (VIa) and 3-oxo-1,2-benzothiazoline-2-(3'-triethylsilyl-2'-propenyl) 1,1-dioxide (VIIa).



(VIa, b)

(VIIa,(b)

PMR spectroscopy indicates that (VIa) comprises 75% of the reaction mixture.

The reaction of several terminal acetylenic hydrocarbons with triethylsilane in the presence of Speier catalyst and iodine proceeds with dehydrocondensation to give silicoacetylenic hydrocarbons [9 10]. However, we did not observe any change in the direction of the hydrosilylation of (III) and the ratio of the regioisomers upon the addition of iodine.

In contrast to triethylsilane, which reacts with (III) upon heating, triethylgermane (II) readily adds to N-propargylsaccharin even at ~20°C in the presence of Speier catalyst in THF. The gem isomer (VIb) is also the predominant product in this case and comprises 80% of the reaction mixture. The yield of the hydrogermylation products and ratio of isomers (VIb) and (VIIb) are not altered when THF is replaced by benzene–hexane and the reaction temperature is raised to 70°C. The reaction proceeds analogously also in the presence of iodine.

The IR spectra of adducts (VIa), (VIb), (VIIa), and (VIIb) contain bands at 1720-1700 (C=O), 1580 (Ph), and 1610-1620 cm^{-1} (–C=C–). The PMR spectral parameters of these compounds are given in Table 1. The assignment of the signals of the isomers was made using the coupling constants of the allyl group and through use of an additive scheme [11]. As a consequence of long-range coupling, the signals of the terminal vinyl protons and methylene group of the gem isomer are broadened. The proton in the cis position to the triethylgermyl group is more shielded than the trans proton. The spectrum of the other isomer is not a first-order spectrum. An additive scheme was used to determine the configuration of this isomer. Comparison of the calculated chemical shifts with the experimental values permitted assignment of trans configuration to adducts (VII).

Thus, a comparative study of the orientation of the trialkylsilane and trialkylgermane in their addition to the triple bonds of 3-O-, 3-S- [1-4], and 3-N-heteroatomic propyne derivatives showed that there is a pronounced predominance of the gem adduct and lack of a marked effect of the nature of the heteroatom in the addend molecule in the case of N-propargylsaccharin. In contrast to the case of their O- and S-propargyl analogs, the addition of triethylsilane (I) and triethylgermane (II) to N-propargylsaccharin proceeds stereoselectively with formation of the trans isomer.

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-567A spectrometer for $CDCl_3$ solutions with TMS as the internal standard. The IR spectra were taken on a UR-20 spectrophotometer.

Preparation of N-Propargylsaccharin (III). A sample of 70 ml DMF and 11.9 g (0.1 mole) propargyl bromide were added with stirring to a mixture of 18.32 g (0.1 mole) saccharin, 13.8 g (0.1 mole) freshly roasted potassium carbonate, and 0.4 g KI. The reaction mixture was heated with stirring for 1.5 h, cooled, poured into cold water, and extracted with ether. The ethereal layer was washed with water and dried over $MgSO_4$ to give 15.3 g (70%) (III), mp 122°C (from ethanol). Found: C, 54.03; H, 3.35; S, 14.80; N, 6.15%. Calculated for $C_{10}H_7NO_3S$: C, 54.30; H, 3.13; S, 14.47; N, 6.33%. IR spectrum (ν, cm^{-1}): 1730 (C=O), 1595 (Ph), 2120 ($-C{\equiv}C-$), 3270 ($\equiv CH-$). PMR spectrum (δ, ppm): 2.37 t (CH), 7.57 m (C_6H_4), 4.53 d (CH_2).

Reaction of (III) with Triethylsilane (I). A mixture of 2.21 g (0.01 mole) N-propargylsaccharin, 1.2 g (0.01 mole) triethylsilane (I), two drops of Speier catalyst (0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol), and 10 ml THF was stirred for 6 h at 70°C. The solvent was removed to give 3.41 g residue, consisting of a 3:1 mixture of (VIa) and (VIIa) as indicated by PMR spectroscopy. Found: C, 57.00; H, 6.10; N, 3.85; S, 9.07; Si, 7.95%. Calculated for $C_{16}H_{21}NSO_3Si$: C, 57.28; H, 6.30; N, 4.17; S, 9.55; Si, 8.37%.

Reaction of (III) with Triethylgermane (II). A mixture of 2.21 g (0.01 mole) N-propargylsaccharin, 1.6 g (0.01 mole) triethylgermane (II), and two drops of Speier catalyst was dissolved in 10 ml THF. The solution was heated for 6 h at 70°C. The reaction mixture was cooled and the solvent was removed to give a 3.81 g residue, consisting of a 5:1 mixture of (VIb) and (VIIb) as indicated by PMR spectroscopy. Found: C, 49.82; H, 5.20; N, 3.12; S, 8.22; Ge, 18.97%. Calculated for $C_{16}H_{21}NSO_3Ge$: C, 50.79; H, 5.56; N, 3.67; S, 8.42; Ge, 19.07%.

LITERATURE CITED

1. A. Kh. Filippova, O. A. Kruglaya, G. S. Lyashenko, V. V. Keiko, I. D. Kalikhman, and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 682 (1976).
2. A. K. Filippova, G. S. Lyashenko, O. A. Kruglaya, V. V. Keiko, I. D. Kalikhman, and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 660 (1977).
3. G. S. Lyashenko, A. Kh. Filippova, I. D. Kalikhman, V. V. Keiko, O. A. Kruglaya, and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 874 (1981).
4. G. S. Lyashenko, A. Kh. Filippova, I. D. Kalikhman, G. G. Naumova, and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2618 (1982).
5. Japanese Patent No. 48-35457 (1973).
6. M. G. Voronkov, G. I. Zelchan, and E. Ya. Lukevits, Silicon and Life [in Russian], Riga (1978).
7. USA Patent No. 4,289,879 (1981).
8. M. G. Voronkov, N. I. Ushakova (Ushakowa), I. I. Tsykhanskaya, and V. B. Pukhnarevich, J. Organomet. Chem., 264, 39 (1984).
9. O. I. Magidson and S. W. Gorbatshaw, Chem. Ber., 56, 1816 (1923).
10. M. G. Voronkov, V. B. Pukhnarevich, N. I. Ushakova, I. I. Tsykhanskaya, A. I. Albanov, and V. Yu. Vitkovskii, Zh. Obshch. Khim., 55, No. 1, 94 (1985).

11. U. E. Matter, C. Pascyai, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, Tetrahedron, 25, 691 (1969).

UNUSUAL REACTION OF NITROSO COMPOUNDS WITH THE BIS(AMINOOXY)METHANE/DIBROMOISOCYANURATE SYSTEM

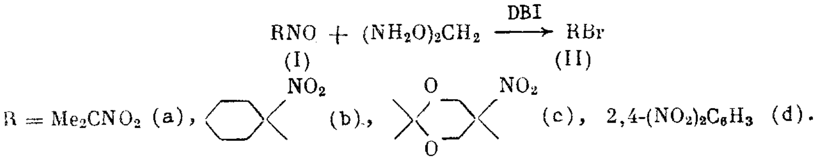
G. A. Smirnov, A. M. Vasil'ev, and O. A. Luk'yanov

UDC 542.91:547.231:547.238

The reaction of nitroso compounds with bis(aminooxy)methane in the presence of dibromoisocyanurate gives the products of the formal replacement of the nitroso group by bromine.

In previous work [1], we have shown that the reaction of various nitroso compounds, including pseudonitrols, with methoxyamine in the presence of dibromoisocyanurate (DBI) gives the corresponding N-methoxydiazene N'-oxides in 10-70% yield.

In an attempt to employ bis(aminooxy)methane (BAM) [2] or its salts instead of methoxyamine, we observed a different pathway for this reaction. Pseudonitrols (Ia)-(Ic) react with BAM to give the products of the formal replacement of the nitroso group by bromine (IIa)-(IIc) in 30-40% yield instead of the expected methylenebis(oxydiazene) oxides.



The reaction of BAM with 2,4-dinitronitrosobenzene gave the corresponding bromide (IId) in only 4% yield.

These nitroso compounds do not react with DBI to give halogen derivatives in the absence of BAM.

Bromides (IIa)-(IId) were identified by comparison with authentic samples by IR and PMR spectroscopy, melting point, and thin-layer chromatography.

EXPERIMENTAL

The IR spectra were taken neat or for KBr pellets on a Specord spectrophotometer. The PMR spectra were taken for $CDCl_3$ solutions on a Tesla BS-467 spectrometer at 60 MHz relative to HMDS as the internal standard.

2-Bromo-2-nitropropane (IIa). a. A sample of 1 g (3.5 mmoles) DBI and 0.26 g (1.7 mmoles) $CH_2(ONH_2)_2 \cdot 2HCl$ were added to a solution of 0.4 g (3.4 mmoles) 2-nitro-2-nitrosopropane (Ia) in 20 ml CH_2Cl_2 at ~20°C, stirred for 6 h, and left overnight. The precipitate was filtered off and the filtrate was evaporated. The residue was subjected to chromatography on silica gel (R_f 0.66 with chloroform as eluent) to give 0.22 g (39%) (IIa) as an oil.

b. A sample of 1.22 g (4.25 mmoles) DBI was added with stirring to a solution of 0.5 g (4.2 mmoles) (Ia) in 20 ml CH_2Cl_2 at ~20°C and then a solution of 0.17 g (2.1 mmoles) $CH_2(ONH_2)_2$ in 20 ml CH_2Cl_2 was added dropwise. The reaction mixture was maintained for 72 h. The precipitate was filtered off and the filtrate was evaporated. The residue was subjected to chromatography to give 0.28 g (39%) (IIa). IR spectrum (ν, cm^{-1}): 3000, 2850, 1550, 1460, 1410, 1390, 1350, 1160, 1110. PMR spectrum (δ, ppm): 2.16 s (6H, 2Me).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2892-2893, December, 1991. Original article submitted March 25, 1991.