SILYLATION OF DIOXANATE OF SILVER SALT OF TRINITROMETHANE WITH DIPHENYLMETHYLCHLOROSILANE AND TRIPHENYLCHLOROSILANE

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We established that, like $(CH_3)_3SiCl$, $(C_6H_5)_2CH_3SiCl$, and $(C_6H_5)_3SiCl$ react with the dioxanate of the Ag salt of trinitromethane (I) at the oxygen reaction center to give the corresponding esters of dinitromethanenitronic acid

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 $\begin{array}{c} R(C_6H_5)_2SiCl + C(NO_2)_3AgO \overbrace{(I)}^{-AgCl} O \xrightarrow{(IO_2)_2C=N} O \\ R = CH_3 (II), \quad C_6H_5 (III) \end{array} \xrightarrow{O} OSi(C_6H_5)_2R \end{array}$

The reaction rate slows up when going from $(CH_3)_3SiCl$ to $R(C_6H_5)_2SiCl$. The structure of nitronic esters (II) and (III) is confirmed by the spectra and some of the chemical transformations. In contrast to the trimethylsilyl ester of dinitromethanenitronic acid (IV), which exists only in solutions, (II) and (III) could be isolated in the pure state. However, the free (II) and (III) quickly decompose with the evolution of nitrogen oxides. In CCl_4 solution, based on the NMR data, (II) decomposes completely in 24 h. Nitronic esters (II) and (III), similar to (IV), enter into the 1,3-cycloaddition reaction with styrene:



The data of the NMR spectra corroborate the structure of (V) and (VI). Treatment of the cycloadducts with alcoholic KOH solution gives the K salt of 1,1-dinitro-3-phenyl-3-propanol (VII). The competing reaction disclosed that (II) and (IV) add to styrene at close rates. As can be seen from Table 1, the chemical shifts of the protons of the ABX system, and the ratios of the spatial isomers of the cycloadducts, are practically independent of the nature of the trialkylsilyl group.

Like (IV), nitronic esters (II) and (III) react with methyl acrylate as silvlation agents, and not by the 1,3-dipolar cycloaddition scheme. The methyl ester of γ , γ , γ -trinitrobutyric acid can be identified after the reaction products are treated with water or aqueous acid solution.

EXPERIMENTAL

All of the experiments with the silvl esters of dinitromethanenitronic acid were run in a dry argon atmosphere using absolute solvents. The NMR spectra were taken on JNM-100 (100 MHz) and Perkin -Elmer R-12 (60 MHz) spectrometers, using HMDS as the standard; the IR spectra were taken on a UR-10 spectrometer. The UV spectra were taken on a Unicam SP-800 spectrophotometer. The GLC analysis

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TABLE 1

Compound (in CD ₃ COCD ₃)	Isomers	Amount in mixture,%	Chemical shifts of protons, ppm					Difference in chemical shifts in isomers, ppm			Spin-spin coup- ling constants, Hz		
			нх	$\mathbf{H}_{\mathbf{A}}$	нB	Si(CH ₃) ₃	C.H.	$\Delta \mathbf{H}_{\mathbf{X}}$	${}^{\Delta H}{}_{A}$	ΔH _B	J_{AX}	J _{BX}	JAB
Adduct of (IV) with styrene	A B	83 17	6,09 5,55	4,39 4,00	3,10 3,75	0,50 0,42	7,35 7,35	0,54	0,39	0,65	8,0 9,3	7,0 7,3	15 14,5
V	Α	79	6,12	4,33	3,15	0,77	7,2	0.55	0.27	0.50	7,5	7,5	15
VI	B A	21 86	5,57 6,03	$3,96\\4,13$	$^{3,74}_{3,05}$	0,72	7,3 mult. 7,2	0,00	0,37	0,58	7,5 7,7	7,5 7,3	—15 —15
	В	·14	5,34	3,98	3,61		mult.	0,09	0,15	0,00	7,7	7,7	14

was run on an LKhM 8M chromatograph (10% of QF deposited on Chromosorb, 151° , carrier gas = helium.

<u>Preparation of Silyl Esters of Dinitromethanenitronic Acid.</u> To 1.73 g of the dioxonate (I) in 7 ml of toluene at (to -5° was added 1.18 ml of $(C_{6}H_{5})_{2}CH_{3}SiCl$, after which the mixture was stirred at 0° for 35 min and then filtered; based on the NMR data, the solution contains (II), 67% yield. After 24 h the (II) in solution decomposes completely, giving $[(C_{6}H_{5})_{2}CH_{3}Si]_{2}O$ (NMR data). A part of the toluene solution of (II) was evaporated in vacuo. Infrared spectrum of (II), cm⁻¹ (in CH₂Cl₂): 860, 1450, 1370, and 1550 (C (NO₂)₂); 1560 (C = N). Ultraviolet spectrum of (II) (in CH₂Cl₂): λ_{max} 305 nm, ε 3700 (the intensity drops rapidly on standing). The free (II) decomposes rapidly with the liberation of nitrogen oxides.

In a similar manner, (III) was obtained from 1.73 g of (I) and 1.5 g of $(C_6H_5)_3SiCl$ in 10 ml of C_6H_6 at 10-20° for 1.5 h. Ultraviolet spectrum (in CH_2Cl_2): λ_{max} 305 nm, ξ 2400 (the intensity decreases on standing).

Reaction of Silyl Esters of Dinitromethanenitronic Acid with Styrene. To 4.5 ml of (II) (from 1.73 g of (I) and 1.18 ml of $(CH_3)(C_6H_5)_2SiCl$ in 7 ml of toluene) was added 1.2 ml of styrene, and after 10 min the solution was filtered and evaporated at 30° (1 mm); the residue was recrystallized from hexane. We obtained 2.08 g of (V), mp 76-78°. Found: N 9.29%. $C_{22}H_{21}N_3O_6Si$. Calculated: N 9.31%. The treatment of 0.3 g of (V) with KCH in alcohol gave 0.2 g of (VII), mp 200-210° (decomp.) (from aqueous alcohol), λ_{max} 378 nm, ϵ 15,100. The acidification of (VII) gives $C_6H_5CH(OH)CH_2CH(NO_2)_2$ (VII), mp 37° (identified by comparison with an authentic sample).

In a similar manner, from 1.73 g of (I) and 1.5 g of $(C_6H_5)_3$ SiCl in 10 ml of C_6H_6 and 1 ml of styrene was obtained 0.67 g of (VI), mp 65-67°. Found: N 7.40%. $C_{27}H_{23}N_3O_6$ Si. Calculated: N 8.19%.

The treatment of 0.48 g of (VI) with KOH in alcohol gave 0.2 g of (VII) as yellow crystals, which, after washing with ether and benzene, melt with decomposition at 150°, λ_{max} 376 nm. Treatment with HCl solution gave (VIII) (which was identified by the NMR spectrum in CCl₄ (δ , ppm): 2.7 triplet (CH₂ and OH); 4.65 triplet CH(OH); 6.25 triplet CH(NO₂)₂; and 7.2 singlet (C₆H₅)).

Reaction of Silyl Esters of Dinitromethanenitronic Acid with Methyl Acrylate. To 3.75 ml of (II) (from 1.73 g of (I) and 1.18 ml of $(CH_3)(C_6H_5)_2$ SiCl in 7 ml of toluene) was added 0.42 ml of methyl acrylate. Evaporation at 30° (1 mm) gave 1.18 g of residue (based on the NMR data, isoxazolidine is absent), which after treatment with water and the usual workup gave 0.84 g of an oil. Based on the GLC and NMR data, the oil contains 0.43 g of $C(NO_2)_3CH_2CH_2COOCH_3$; 3.4 singlet (OCH₃); 3.0 multiplet (CH₂C(NO₂)₃); 2.4 ppm, multiplet (CH₂COOCH₃).

In a similar manner, from (III) (obtained from 1.73 g of (I) and 1.5 g of $(C_6H_5)_3$ SiCl in 10 ml of C_6H_6) and 0.48 ml of methyl acrylate was isolated 1.8 g of an oil, which was free of 2-triphenylsilyloxy-3,3-dinitro-5-carbomethoxyisoxazolidine. After treatment with dilute HCl solution, a certain amount of $C(NO_2)_3$ \cdot CH₂CH₂COOCH₃ was detected in the reaction products by GLC.

Competing Reaction of (IV) and (II) with Styrene. To a mixture of 0.9 mmole of (IV) and 0.9 mmole of (II) in 7 ml of toluene was added 1 mmole of styrene. Based on the NMR data, after 5 min 0.47 mmole of (V) and 0.48 mmole of 2-trimethylsilyloxy-3,3-dinitro-5-phenylisoxazolidine are formed, and equimolar amounts of the starting o-esters remain.

CONCLUSIONS

1. The silylation of the dioxanate of the Ag salt of trinitromethane with diphenylmethylchlorosilane and triphenylchlorosilane respectively gives the diphenylmethylsilyl and triphenylsilyl esters of dinitromethanenitronic acid.

2. The obtained nitronic esters enter into the 1,3-cyclo-addition reaction with styrene, giving the corresponding 5-phenyl-substituted isoxazolidines.

3. The obtained nitronic esters react with methyl acrylate not as dipoles, but as silylation agents.