NONAQUEOUS CONDENSATION OF SILYLATED C- AND N-NITRO COMPOUNDS WITH TRIMETHYLSILOXYMETHYLDIALKYLAMINES

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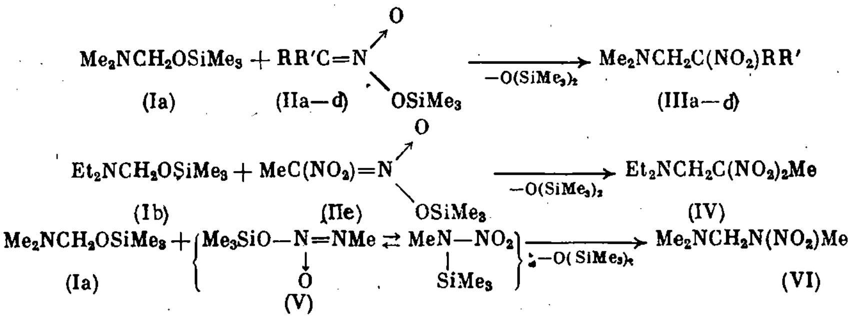
Silyl esters of nitronic acids (SENA) [1-4] are commonly used in organic synthesis since they permit substantial alteration of the conditions for several known reactions. Thus, the Henri reaction was recently carried out using SENA in nonaqueous media [5, 6].

In the present work, we demonstrated the possibility of carrying out the Mannich reaction of silylated C- and N-nitro compounds with trimethylsiloxymethyldialkylamines (Ia) and (Ib).* SENA (IIa-e) and trimethylsilylmethylnitramine (V) condense smoothly and quantitatively with (Ia) and (Ib) in aprotic nonpolar solvents or in the absence of solvent:



$$Me_2NCH_2OSiMe_3 + RR'C{=}N(\rightarrow O)OSiMe_3 \xrightarrow[-O(SiMe_3)_2]{} Me_2NCH_2C(NO_2)RR'$$

(Ia) (IIa–d) (IIIa–d)

$$Et_2NCH_2OSiMe_3 + MeC(NO_2){=}N(\rightarrow O)OSiMe_3 \xrightarrow[-O(SiMe_3)_2]{} Et_2NCH_2C(NO_2)_2Me$$

(Ib) (IIe) (IV)

$$Me_2NCH_2OSiMe_3 + \left\{ Me_3SiO{-}\underset{\downarrow O}{N}{=}NMe \rightleftarrows MeN(SiMe_3){-}NO_2 \right\} \xrightarrow[-O(SiMe_3)_2]{} Me_2NCH_2N(NO_2)Me$$

(Ia) (V) (VI)

R = H, R' = Me (a); R = R' = Me (b); R = R' = NO_2 (c); R = H, R' = COOMe (d).

Reactions (1)-(3) are accelerated by Lewis bases such as $SnCl_4$.

PMR spectroscopy indicates the lack of the products of the O-alkylation of SENA and (V) and any derivatives arising from such products in the product mixtures of reactions (1)-(3). This finding indicates that ambident sinylnitronates (IIa-e) and (V) react with (I) exclusively at the carbon atom or, correspondingly, at the nitrogen atom bearing the NO_2 group.

The method of carrying out nonaqueous Mannich condensation proposed in this work permits the synthesis of products which could be obtained by conventional methods only with difficulty or not at all. This is primarily found for products which are unstable in aqueous media. Thus, for example, (IIId) upon dissolving in water, ethanol, or DMSO decomposes completely. The IR spectrum of (IIId) shows νCO (stretching) 1640 cm^{-1} and the lack of bands for the covalent NO_2 group. On the other hand, the IR spectrum of (IIId) has strong bands at 1280-1450 cm^{-1} which indicate the betaine structure $Me_2N^{+}HCH_2C^{-}(NO_2)CO_2Me$. The $[RO_2CC(NO_2)_2]^{-}$ anion has ν_{as} 1284 and νCN 1446 cm^{-1} [8].

EXPERIMENTAL

The preparation of (I)-(VI) was carried out in an inert-gas atmosphere in dry solvents.

2-Nitro-4-methyl-4-azapentane (IIIa). A sample of 1.5 g (IIa) [1] was added with stirring to 1.5 g (Ia) [7] in 2 ml CH_2Cl_2 at 25°C, and the mixture was cooled to 0°C. Then, about 0.2 ml $SnCl_4$ was added in vacuum (spontaneous heating was noted), and the mixture was dis-

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*The capacity of (Ia) and (Ib) to undergo condensation with trimethylsilyl derivatives of weak CH and NH acids was reported in our previous work [7].

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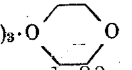
tilled in vacuum to give 1.25 g (95%) (IIIa), bp 65-66°C (8 mm) [9]. PMR spectrum (CH_2Cl_2, δ, ppm): 1.45 d (MeC), 2.22 g (MeN), 2.4-3.2 (CH_2), 4.5-5.0 m (CH).

2,4-Dimethyl-2-nitro-4-azapentane (IIIb). A sample of 2 g (IIb) was added stirring to 1.76 g (Ia) (spontaneous warming was noted), and the mixture was fractionated in vacuum after 30 min to give 1.53 g (97%) (IIIb), bp 65-66°C (10 mm) [10]. PMR spectrum in CH_2Cl_2 (δ, ppm): 1.53 s (MeC), 2.25 s (MeN), 2.8 s (CH_2).

1,1,1-Trinitro-4-methyl-3-azabutane (IIIc). A sample of 1.35 g Me_3SiCl was added with stirring to 4.32 g $AgC(NO_2)_3$· in 30 ml toluene at −10°C and maintained at this temperature for 30 min [3]. Then, 1.83 g (Ia) was added with vigorous stirring, and the mixture was warmed to 20°C. AgCl (1.76 g) was separated, and the filtrate was evaporated at 20 mm Hg. The residue was distilled to yield 2.2 g (85%) (IIIc) with bp 56-58°C (0.5 mm), n_D^{20} 1.4994. PMR spectrum in CH_2Cl_2 (δ, ppm): 2.50 s (MeN), 4.10 s (CH_2). Found: C 22.66; H 3.61; N 26.90%. $C_4H_8N_4O_6$. Calculated: C 23.00; H 3.85; N 26.90%.

Methyl Ester of 2-Nitro-3-dimethylaminopropionic Acid (IIId). A sample of 0.58 g (IId) [2] was added with stirring to 0.5 g (Ia) in 3 ml CH_2Cl_2 at 0°C. The precipitate was filtered off, washed with CH_2Cl_2, and dried at 1 mm Hg to yield 0.52 g (96%) (IIId), mp 82-83°C. This product is insoluble in CH_2Cl_2, ether, benzene, and acetonitrile, and it decomposes in water, methanol, and DMSO. Found: C 40.95; H 6.75; N 16.21%. $C_6H_{12}N_2O_4$. Calculated: C 40.91; H 6.82; N 15.91%.

3,5-Dinitro-3-ethyl-3-azahexane (IV). A sample of 1.46 g Ib) was added with stirring at −10°C to a solution of (IId) obtained from 1 g 1,1-dinitroethane and 2.4 g N,N-diphenyl-N-trimethylsilylurea [4] in 5 ml CH_3Cl, and the solution was warmed to 25°C. The precipitate was removed. The solvent was distilled off, and the residue was fractionated to yield 1.1 g (65%) (IV), bp 58°C (<0.1 mm), n_D^{20} 1.4530 [11]. PMR spectrum in CCl_4 (δ, ppm): 0.98 t ($\underline{Me}CH_2$), 2.13 s [$MeC(NO_2)_2$], 2.65 q ($Me\underline{CH_2}$), 3.58 s [$CH_2C(NO_2)_2$].

2-Nitro-4-methyl-2,4-diazapentane (VI). A sample of 2 g (V) [12] was slowly added to 1.98 g (Ia) at 0°C. The reaction mixture was evaporated at 20 mm Hg and fractionated to yield 1.7 g (VI), bp 46-48°C (0.3 mm), mp ~20°C. Found: C 35.63; H 8.10; N 31.42%. $C_4H_{11}N_3O_2$. Calculated: C 36.01; H 8.27; N 31.5%.

CONCLUSIONS

The reaction of trimethylsiloxymethyldialkylamines with silylnitronates as well as with trimethylsilylmethylnitramine in aprotic solvents or without solvent leads to the normal Mannich condensation products.

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