Preparation of some 4-Substituted Selenosemicarbazides

CARL Th. PEDERSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, Copenhagen, Denmark

Some new 4-substituted selenosemicarbazides have been prepared with the purpose of comparing their infrared spectra with the spectra of the corresponding thiosemicarbazides [1] and trying to synthesise the hitherto unknown 1,2,3,4-selenatriazoles. The latter attempt has, however, been unsuccessful.

The 4-substituted selenosemicarbazides were prepared by reacting the corresponding isoselenocyanates with various hydrazines. Only a very few isoselenocyanates are known [2-5]; they have mostly been prepared by the reaction between isocyanides and elementary selenium. Triphenylmethyl isoselenocyanate was obtained from triphenylmethyl chloride and potassium selenocyanate; it has been described by Rheinboldt [6] as a selenocyanate, but was shown by Tarantelli and Pecile [7] to be the iso-compound.

By boiling diphenylmethyl bromide, potassium thiocyanate and anhydrous zinc chloride in dry acetone, diphenylmethyl isothiocyanate was formed in 87 % yield. By boiling diphenylmethyl bromide and potassium selenocyanate in dry acetone, the selenocyanate was formed in a yield of 70 %. Its constitution is established by its infrared spectrum which shows a very sharp band at 2140 cm^{-1}. Diphenylmethyl thiocyanate shows a sharp band at precisely the same position, this band being characteristic of the SCN-group [8,9]. Triphenylmethyl isoselenocyanate has a broad band near 2100 cm^{-1}. The structure of the diphenylmethyl compound is further confirmed by the fact that it does not react with hydrazine. An attempt to isomerise it by refluxing its acetone solution with zinc chloride was unsuccessful.

Experimental. Cyclohexyl isoselenocyanate. Cyclohexyl isocyanide was prepared as described by Ugi and Meyer [10] from N-cyclohexylformamide. The isocyanide was dissolved in chloroform; red selenium was added and the mixture was refluxed for 16 h. The unreacted selenium was filtered and the chloroform was removed *in vacuo* at 50°C. The residue was a light brown liquid with a pleasant esterlike smell. After inhalation for a short time it produced a burning feeling in nose and throat. As it is known that isoselenocyanates are very thermolabile and can only be distilled with great loss, it was used without further purification.

Triphenylmethyl isoselenocyanate. Triphenylmethyl chloride (3.6 g) and potassium selenocyanate (1.8 g) were dissolved in dry acetone (50 ml). The mixture was allowed to stand at room temperature for 3 h; the precipitated potassium chloride was filtered off and the solution evaporated almost to dryness *in vacuo* at approximately 40°C. Yield 2.8 g (63 %). The compound was recrystallised from hexane. M.p. 127.5–129°C.

Diphenylmethyl selenocyanate. A solution of potassium selenocyanate (1.3 g) and diphenylmethyl bromide (2.2 g) in dry acetone (50 ml) was refluxed for 4 h. The acetone was removed *in vacuo* at 40°C. The residue was a light yellow oil which solidified on cooling in ice. Yield 1.7 g (70 %), recryst. from hexane m.p. 68–69°C. (Found: C 61.62; H 4.17; N 5.18. Calc. for $C_{14}H_{11}NSe$: C 61.80; H 4.05; N 5.16).

A solution of 1 g of this compound, together with 0.5 g of anhydrous zinc chloride in dry acetone, was refluxed for 3 h during which the solution turned dark brown. After evaporation of the acetone a black tarry residue was left, an ether extract of which gave no precipitate of a selenosemicarbazide by addition of hydrazine.

The selenosemicarbazides (Table 1). The 4-cyclohexylselenosemicarbazides were prepared by dissolving the isoselenocyanate in ethanol and adding the calculated amount of hydrazine; an exothermic reaction immediately takes place. The compounds were recrystallised from ethanol.

The 4-triphenylmethylselenosemicarbazides are prepared by shaking a solution of the isoselenocyanate in cyclohexane with a little more than the calculated amount of hydrazine. Cyclohexane is used because the isoselenocyanate is decomposed in polar solvents. The selenosemicarbazides were recrystallised from ethanol.

Attempts to prepare 5-alkyl (or aralkyl) amino-1,2,3,4-selenatriazoles. The mono-(4)-substituted selenosemicarbazides were suspended in glacial acetic acid and cooled to 0°C, and a concentrated solution of sodium nitrite in water was added slowly with stirring. On addition of the first drop of the nitrite solution red selenium was precipitated with evolution of gas. When the calculated amount of nitrite had been added the selenium was filtered off. The small amount of oil which

Table 1. Selenosemicarbazides, $R^4NH-CSe-NR^3NR^2R^1$.

R^4	R^3	R^2	R^1	Yield * %	M.p., °C	Formula	Analyses					
							C		H		N	
							Found	Calc.	Found	Calc.	Found	Calc.
C_6H_{11}	H	H	H	47	156–157	$C_7H_{15}N_3Se$	38.13	38.21	6.84	6.87	19.20	19.10
C_6H_{11}	H	CH_3	CH_3	66	148–149	$C_9H_{19}N_3Se$	43.40	43.58	7.51	7.72	16.98	16.95
C_6H_{11}	H	H	C_6H_5	55	149–150	$C_{13}H_{19}N_3Se$	52.65	52.75	6.48	6.47	14.38	14.20
$(C_6H_5)_3C$	H	H	H	92	169–170	$C_{20}H_{19}N_3Se$	62.95	63.19	4.65	5.00	11.22	11.05
$(C_6H_5)_3C$	CH_3	H	H	71	176–176.5	$C_{21}H_{21}N_3Se$	64.05	64.02	5.32	5.21	10.87	10.67
$(C_6H_5)_3C$	CH_3	CH_3	CH_3	58	184–184.5	$C_{23}H_{25}N_3Se$	65.30	65.30	6.24	5.97	9.94	9.85

* The yields of the cyclohexyl compounds are based on the isocyanide, those of the triphenylmethyl compounds on the isoselenocyanate.

separated on dilution of the filtrate with water was found to contain no selenium.

The reaction was also tried with unsubstituted selenosemicarbazide prepared according to Huls and Renson[11] with the same result.

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Photochemical Studies

I. The Photorearrangement of Quinoline-N-oxide

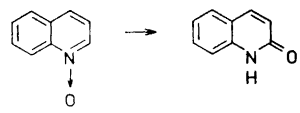
O. BUCHARDT

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, Copenhagen, Denmark

Photochemical isomerizations of tertiary amine-N-oxides and a few related compounds have been known for some time[1-5], but the scope and variety of these reactions have not been investigated further.

On irradiation of a solution of quinoline-N-oxide in absolute ethanol a white crystalline precipitate was formed, which was almost insoluble in most organic and inorganic solvents. After isolation of the precipitated compound (I), the filtrate on evaporation of the solvent yielded a crystalline residue (II) which, after recrystallization, melted at 197–198°C. Elementary analysis and molecular weight established the empirical formula of (II) as C_9H_7NO, an isomer of the starting material (m.p. 57–58.5°C).

If quinoline-N-oxide rearranges in the same manner as quinoxaline-N-oxide and quinoxaline-N,N′-dioxide[1,2], it would give carbostyril (II):



II

The melting point of the rearranged product corresponds to that of carbostyril, and the ultraviolet, infrared and nuclear magnetic resonance spectra showed no difference from spectra of an authentic sample of carbostyril. The 60 Mc/sec nuclear magnetic resonance spectrum (20% in trifluoroacetic acid with tetramethylsilane as internal reference) consisted of three peaks: a broad peak at 770 cps (amide proton), two doublets at 527 cps and 448 cps (olefinic protons), and a strong multiplet at 480 cps (aromatic protons).

The other product (I) which was insoluble in ethanol melted at *ca.* 300°C under sublimation. Elementary analysis and molecular weight corresponded to the formula $C_{18}H_{14}N_2O_2$. The presence of a nonconjugated-CO-NH-group was strongly indicated by the infrared spectrum which showed carbonyl absorption at 1715 cm^{-1}, whereas carbostyril and other conjugated lactams show carbonyl absorption at 1680–1630 cm^{-1} [6]. On sublimation the compound was almost quantitatively reconverted to carbostyril, and these results together with spectroscopical and analytical data suggested that it was a dimer of carbostyril, initially formed by the rearrangement of quinoline-N-oxide. To prove this, a solution of carbostyril in absolute ethanol was irradiated. This gave almost quantitatively a crystalline precipitate which was shown to be identical with (I), by infrared and nuclear magnetic resonance spectra.

It is known [7-9] that 2-pyridones and N-methylcarbostyril dimerize, and the 2-pyridone dimers have been assigned