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LETTERS TO THE EDITOR

Synthesis of Enhydrazides Derived from Unsaturated Carboxylic Acids and Their Reactions with Electrophilic Reagents

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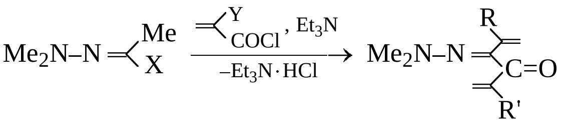
Earlier we showed that acetyl- and benzoyl-substituted enhydrazides derived from 1,1-dimethylhydrazines react with phosphorus pentachloride to give acyclic and cyclic organophosphorus compounds [1]. Enhydrazides derived from 1,1-dimethylhydrazine with unsaturated acyl radicals have been unknown, even though they, comprising an electrophilic and a nucleophilic double bonds, show promise as monomers and polyfunctional synthons.

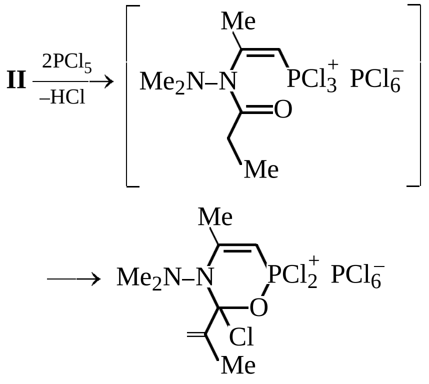
We found that acetaldehyde and acetone *N,N*-dimethylhydrazones react with acryloyl and methacryloyl chlorides in the presence of bases to give enhydrazides **I** and **II**.



I, II

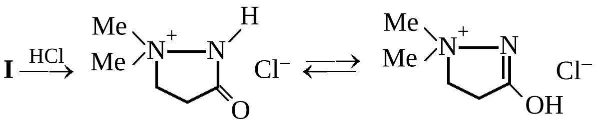
R = R' = H (**I**), Me (**II**).

Methacrylic 1-isopropenyl-2,2-dimethylhydrazide (**II**) reacts with phosphorus pentachloride, yielding an oily substance which is insoluble in benzene. The ^{31}P NMR spectrum of the phosphorylation product contains two signals at –296.5 (PCl_6^-) and 54.7 ppm, d (chlorophosphonium cation), $^2J_{PH}$ 35.4 Hz. The position of the doublet is characteristic of six-membered heterocycles [2]. Probably, the phosphorylation of compound **II** stops, by steric reasons, on the stage of intermediate **III**, and the intramolecular oxygen transfer we observed earlier in phosphorylations of enhydrazides with small acyl substituents [1] has no time to complete.



III

To find out, if the hydrogen chloride liberated in the course of phosphorylation takes part in side reactions with enhydrazides **I** and **II**, we reacted HCl with acrylic 2,2-dimethyl-1-vinylhydrazide (**I**) in carbon tetrachloride. The resulting colorless crystalline substance which, on the basis of the elemental analysis and ^{1}H NMR spectrum, was assigned the structure of 1,1-dimethyl-3-oxopyrazolidinium hydrochloride (**IV**), i.e. under the action of HCl the enhydrazide molecule loses an *N*-alkenyl group. The ^{1}H NMR spectrum of the heterocycle does not exclude that the product has an admixture of enol tautomer **V**.



IV **V**

The structure of compound **IV** was proved by its independent synthesis by the acylation of 1,1-dimethylhydrazine with acryloyl chloride by the procedure in [3]. Thus, to suppress the side reaction enhydrazides are expedient to phosphorylate with si-

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multaneous effective removal from the reaction medium of hydrogen chloride.

Enhydrazides I and II. A solution of 3 g of acetaldehyde 1,1-dimethylhydrazone and 3.5 g of triethylamine in 40 ml of benzene was added dropwise with stirring to a solution of 3.2 g of acryloyl chloride in 30 ml of benzene. After 1 h, the triethylamine hydrochloride precipitate was filtered off, and the filtrate was distilled in a water-jet-pump vacuum. Enhydrazide **I**. Yield 3 g (62%), bp 80°C (18 mm), n_D^{20} 1.4932. ^{1}H NMR spectrum, δ, ppm: 2.80 s (6H, Me_2N), 4.75 s, 5.00 s (2H, CH_2=CHN), 6.95 s (1H, CH_2=C*H*N), 5.74 s, 6.40 s (2H, CH_2=CHCO), 7.10 s (1H, CH_2=C*H*CO). Found, %: C 60.08; H 8.31; N 19.12. $C_7H_{12}N_2O$. Calculated, %: C 60.00; H 8.57; N 20.00.

Enhydrazide **II** was obtained in a similar way from 4 g of acetone 1,1-dimethylhydrazone, 4.05 g of triethylamine, and 4.2 g of methacryloyl chloride, yield 4.9 g (73%), bp 35°C (2 mm), n_D^{20} 1.4692. ^{1}H NMR spectrum, δ, ppm: 1.94 s (6H, MeS=), 2.71 s (6H, Me_2N), 4.69 s, 5.04 s (2H, CH_2=CH), 4.88 s, 5.20 s (2H, CH_2=CCO). Found, %: C 64.11; H 9.07; N 16.32. $C_9H_{16}N_2O$. Calculated, %: C 64.29; H 9.54; N 16.67.

Reaction of enhydrazide II with PCl_5. A solution of 1 g enhydrazide **II** in 10 ml of benzene was added dropwise with stirring to a solution of 2.6 g of PCl_5 in 30 ml of benzene. The solution got turbid, and compound **III** separated within some hours as a light yellow oily noncrystallizing material. It was washed with benzene and dried in a vacuum, yield 1.4 g (43%).

1,1-Dimethyl-3-oxopyrazolidinium chloride (IV). *a*. Dry HCl was passed through a solution of 0.5 g of enhydrazide I in 2 ml of CCl_4 for 10 min. Compound **IV** separated as crystals and was filtered off and dried in a vacuum. Yield 0.25 g (56%), mp 195–197°C. ^{1}H NMR spectrum, δ, ppm: 2.82 t (2H, CH_2CO, $^3J_{HH}$ 8.0 Hz), 3.29 s (Me_2N^+), 3.94 t (2H, CH_2N^+, $^3J_{HH}$ 8.0 Hz). Found, %: C 39.88; H 7.63; Cl 24.29; N 18.11. $C_5H_{11}ClN_2O$. Calculated, %: C 39.87; H 7.31; Cl 23.59; N 18.60.

b. Dimethylhydrazine, 1.7 g, was added with stirring to an ice-cooled solution of 2.6 g of acryloyl chloride in 40 ml of diethyl ether. Compound **IV** separated as a colorless viscous material. After 2 h it was fitered off and recrystallized from dimethylformamide. Yield 1.5 g (35%), mp 196–197°C. The ^{1}H spectrum of the product coincides with the spectrum of heterocycle **IV** obtained by method *a*.

The ^{1}H and ^{31}P NMR spectra in $CDCl_3$ and DMSO were measured on a Bruker DPX-400 spectrometer at 400 and 161.98 MHz, respectively, internal reference TMS.

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