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Abstract

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THE SIMPLEST UNSATURATED DIALKYLHYDRAZONES

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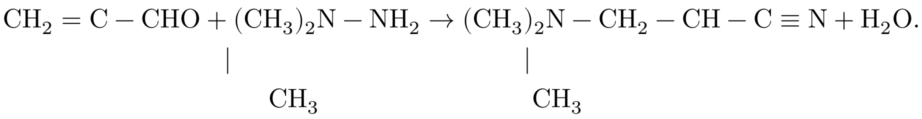
We have previously shown (^{1}) that the condensation of acrolein with unsymmetrical dialkylhydrazines in a weakly acidic medium in the cold leads, instead of the expected unsaturated N,N-dialkylhydrazones, to β-dialkylaminopropionitriles:

$$R_2N-NH_2+CH_2=CH-CHO\rightarrow H_2O+R_2N-CH_2-CH_2-C\equiv N \quad (1)$$

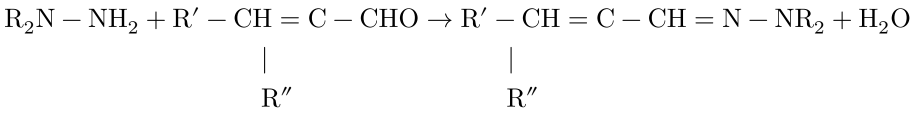
$$(R=CH_3,\ C_2H_5).$$

It was of considerable interest to determine how widespread this rearrangement is. To this end we studied the interaction with dialkylhydrazines of the nearest isomeric homologs of acrolein—crotonaldehyde and α-methylacrolein. However, the "aminonitrile rearrangement" (1), which proceeds readily with acrolein, was observed for its homologs under the same conditions in only one case, and even then only as a side reaction. From the products of condensation of α-methylacrolein with dimethylhydrazine, β-dimethylaminoisobutyronitrile was isolated in low yield:



$$CH_2=\underset{\underset{CH_3}{|}}{C}-CHO+(CH_3)_2N-NH_2\rightarrow(CH_3)_2N-CH_2-\underset{\underset{CH_3}{|}}{CH}-C\equiv N+H_2O. \quad (2)$$

The main products were previously unknown unsaturated N,N-dialkylhydrazones:



$$R_2N-NH_2+R'-CH=\underset{\underset{R''}{|}}{C}-CHO\rightarrow R'-CH=\underset{\underset{R''}{|}}{C}-CH=N-NR_2+H_2O \quad (3)$$

(R′ and R″ = H or CH_3)

The simplest unsaturated ketone—methyl vinyl ketone—under the same conditions, with diethylhydrazine, forms the normal reaction product analogously to (3), whereas with dimethylhydrazine, instead of a hydrazone, it gives a water-soluble high-molecular compound, which was not studied further. It should be noted that polymer formation occurred in all cases, somewhat lowering the yields.

The characteristics of the unsaturated dialkylhydrazones first synthesized by us are given in Table 1.

Their structure was proved by hydrolysis in an acidic medium to the starting carbonyl compounds, as well as by data on characteristic frequencies in the infrared spectra.

The unsaturated hydrazones obtained are the simplest known compounds with the grouping $C = C - C = N - N$, which is of considerable interest as an example of very poorly studied p-π-π-conjugated systems. As can be seen from the data in Table 1, the conjugated system $C = C - CH = N - N$ (i.e., in aldehyde hydrazones) is characterized by extremely high exaltations of refraction and very large dispersion, which until now have been observed only in systems with three conjugated multiple bonds ($E\Sigma_D$ 3.3-3.4 and $\omega_{FCD} \sim 51$ (^{2})).

Table 1

α,β-Unsaturated N,N-dialkylhydrazones

N,N-Dialkylhydrazone	Empirical formula	b.p., °C (pressure, mm)	d_4^{20}	n_D^{20}	Δ^{20}_{F-C}	MR_D, found	MR_D, calc.*	Refraction exaltation EM_D	Refraction exaltation $E\Sigma_D$	ωFCD	C, %, found	C, %, calc.	H, %, found	H, %, calc.	N, %, found	N, %, calc.	Yield, %
Dimethylhydrazone of α-methylacrolein	$C_6H_{12}N_2$	56 (29)	0.8491	1.5052	162.6	39.18	35.75	3.43	3.06	51.99	64.41; 64.36	64.25	11.19; 11.12	10.77	24.70; 24.87	24.98	45**
Diethylhydrazone of acetaldehyde	$C_8H_{16}N_2$	67.8–68.5 (15)	0.8451	1.4992	144.5	48.71	45.03	3.68	2.62	48.99	68.79; 68.64	64.52	11.95; 11.56	11.50	20.26; 20.11	19.98	65

N,N-Dialkylhydrazone	Empirical formula	b.p., °C (pressure, mm)	d_4^{20}	n_D^{20}	$\Delta^{20} F_C$	MR_D, found	MR_D, calc.*	Refraction exaltation EM_D	Refraction exaltation $E\Sigma_D$	ωFCD	C, %, found	C, %, calc.	H, %, found	H, %, calc.	N, %, found	N, %, calc.	Yield, %
Dimethylhydrazone of crotonaldehyde	$C_6H_{12}N_2$	70–71 (29)	0.8511	1.5152	275.3	39.70	35.75	3.94	3.52	54.02	64.45, 64.40	68.25	11.04, 11.03	10.77	25.15, 25.02	24.98	65
Diethylhydrazone of crotonaldehyde	$C_8H_{16}N_2$	78.5–79.5 (15)	0.8501	1.5082	251.0	49.17	45.03	4.14	2.95	49.40	68.97, 68.82	68.52	11.73, 11.67	11.50	19.77, 19.98	19.98	73
Diethylhydrazone of methyl vinyl ketone	$C_8H_{16}N_2$	46.3–46.8 (15)	0.8281	1.4614	119.1	46.47	45.03	1.44	1.03	35.15	68.61, 68.38	68.52	11.69, 11.38	11.50	19.99, 20.19	19.98	30

* According to the refractions of the bonds of Fogel.
** The yield and analytical data are given for the fraction 55–57° (29 mm).

It is very interesting and specific for a conjugated system of this type that there is a sharp difference in the effects of a central disturbance of conjugation depending on the position of the side chain. In compounds with a central disturbance of conjugation at the $C = C$ bond (hydrazones of α-methylacrolein), there is observed, as usual, a small decrease in molecular refraction and dispersion in comparison with the unbranched isomers (hydrazones of crotonaldehyde). At the same time, disturbance of conjugation at the $C = N$ bond (in the hydrazone of methyl vinyl ketone) leads to an unusually strong depression of refraction and dispersion, which decrease to values typical for systems with two conjugated bonds, i.e., in this case the effect of p-π-conjugation is practically completely reduced.

Experimental Part

The starting substances were purified before being introduced into the reaction by distillation on a Vigreux column with an efficiency of 15 theoretical plates.

The aldehydes and methyl vinyl ketone were stabilized with a small addition of hydroquinone.

α-Methylacrolein* after distillation had the following constants: b.p. 68.0–68.2° (758 mm); d_4^{20} 0.8389; n_D^{20} 1.4154.

Crotonaldehyde was obtained by condensation of acetaldehyde (^{3}): b.p. 102.0–102.2° (763 mm); d_4^{20} 0.8525; n_D^{20} 1.4373.

Methyl vinyl ketone was synthesized by the reaction of acetone with paraform (^{4}): b.p. 79.5–80.5° (760 mm); d_4^{20} 0.8631; n_D^{20} 1.4053.

Dimethylhydrazine and diethylhydrazine were the same as in the preceding paper (^{1}).

Interaction of dialkylhydrazines with carbonyl compounds. 78 g (0.5 mole) of $NaH_2PO_4 \cdot 2H_2O$ (chemically pure) was dissolved in 150 ml of water, and 0.5 mole of dialkylhydrazine was added in the cold. To the resulting salt, over the course of 15–20 min, 0.5 mole of the carbonyl compound was added with constant shaking and cooling with water. After 30 min the mixture was saturated with KOH; the organic layer was separated, dried over alkali, and distilled on a Vigreux vacuum column of 12 theoretical plates efficiency. In the case of reaction with methyl vinyl ketone, upon addition of alkali a rapid darkening and resinification of the organic layer was observed. In this experiment, as also with dimethylhydrazine, no products other than resin could be isolated. In all the other experiments, the main distillation fractions were the result of normal condensation (3)—hydrazones.

α,β-Unsaturated N,N-dialkylhydrazones are oily yellowish liquids with a pungent odor, poorly soluble in water; they do not reduce Fehling' s solution on boiling. They are very weak monoacidic bases, titrated without a distinct transition in the presence of bromophenol blue. On brief boiling with 6 N aqueous solutions of mineral acids, the hydrazones are readily hydrolyzed to the initial carbonyl compounds, which, for identification, were distilled off into a solution of 2,4-dinitrophenylhydrazine or semicarbazide. The melting points of the derivatives obtained after hydrolysis and prepared from the original aldehydes and ketones coincided (see Table 2).

Table 2

Melting points (°C) of derivatives of carbonyl compounds obtained after hydrolysis of dialkylhydrazones

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* We express our gratitude to A. M. Kutyn and M. A. Korshunov for kindly providing the preparation.

Initial hydrazone	Derivative	Substance under study	Authentic substance	Literature data (5)
Dimethylhydrazone of α-methylacrolein	Semicarbazone	195-196	195-196	198
Diethylhydrazone of α-methylacrolein	Semicarbazone	194-195	195-196	198
Dimethylhydrazone of croton-aldehyde	2,4-Dinitrophenylhydrazone	188-189	188-189	190
Diethylhydrazone of croton-aldehyde	2,4-Dinitrophenylhydrazone	186-188	188-189	190
Diethylhydrazone of methyl vinyl ketone	Semicarbazone	138-240	139-142	141

Infrared spectra, recorded on a UR-10 double-beam automatic spectrophotometer with a layer thickness of 25 μ in the region 700-4000 cm^{-1}, confirm the structure of the hydrazones obtained.

In all cases, strong absorption bands were found at 1570-1587 cm^{-1}, which should be assigned to stretching vibrations of the C=N bond in dialkylhydrazones (1575-1616 cm^{-1} according to data (6)). At the same time, the spectra lack absorption bands of multiple C=O bonds (in the region 1650-1750 cm^{-1}) and C N (in the region around 2250 cm^{-1}). The preservation of carbon-carbon double bonds and their positions is demonstrated by the presence of absorption bands of C=C stretching vibrations at 1622-1646 cm^{-1}, which coincides with the interval 1621-1647 cm^{-1} reported in the literature (7) for α,β-unsaturated carbonyl compounds. In addition, in the spectra of the hydrazones of methacrolein there are bands of stretching vibrations of terminal groups $>C=CH_2$ at 3087-3088 cm^{-1} (3077-3092 cm^{-1} according to (7)) and the corresponding deformation vibrations at 899-901 cm^{-1} (885-895 cm^{-1} according to (7)). In the hydrazones of crotonaldehyde, bands of stretching and deformation vibrations of C–H in the –CH=CH–grouping (trans) were found, respectively, at 3012-3021 cm^{-1} and 973-974 cm^{-1} (according to literature data (7), 3010-3040 cm^{-1} and 960-970 cm^{-1}). In the spectrum of the diethylhydrazone of methyl vinyl ketone there are two pairs of bands corresponding to stretching (3030 and 3092 cm^{-1}) and deformation (940 and 995 cm^{-1}) vibrations of the hydrogen atoms of vinyl groups.

β-Dimethylaminoisobutyronitrile. Aminonitriles, which boil above the unsaturated hydrazones isomeric with them and have much lower refractive indices, had to be sought in the distillation fractions following the hydrazone fractions. A small amount of such a fraction was found only in the condensation of α-methylacrolein with dimethylhydrazine. After three distillations, 9 g of the combined fractions from three replicate experiments carried out under analogous conditions gave 0.8 g of a colorless mobile liquid with a weak amine odor and b.p. 78.0–78.5° (30 mm); n_D^{20} 1.4259. Literature data for β-dimethylaminoisobutyronitrile (^{8}): b.p. 55–56° (6 mm); n_D^{25} 1.4210.

Found, %: N 24.70; 24.83
$C_6H_{12}N_2$. Calculated, %: N 24.98

The substance is sharply titrated with 0.1 N aqueous HCl. Found: E 117; 118. $C_6H_{12}N_2$. Calculated: E 112.2.

In the infrared spectrum of the substance, an intense band at 2247 cm^{-1}, characteristic of the nitrile group, was found.

Passing a stream of dry hydrogen chloride through an ethereal solution of the substance gave a white precipitate of the hydrochloride. After recrystallization from an ethyl acetate–methyl alcohol mixture, the hydrochloride melted at 169–171°. Literature data for β-dimethylaminoisobutyronitrile hydrochloride: m.p. 171–172° (^{8}).

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