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SODIUM SALTS of ACYLHYDRAZONES OF 1,3 - DIOXOCOMPOUNDS AND THEIR ACYLATION

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Abstract: Sodium salts of acylhydrazones of 1,3-dioxo-compounds react with acylchlorides yielding (E)-β-keto-enehydrazides (as a result of N-acylation). The respective acetylacetone and aroylacetone N-acyl-derivatives showing the equilibrium between (E)- and (Z)-isomers convert into 1-acyl-5-acyloxy-2-pyrazolines.

Whereas stable sodium salts of simple 1,3-dioxo-compounds are well known and have been widely used as starting materials for reactions with electrophiles (acylation, alkylation etc.), their nitrogen analogs, sodium salts of 1,3-ketoaldehyde and 1,3-diketone imines, oximes, hydrazones etc., which could have similar synthetic applications, are unknown.

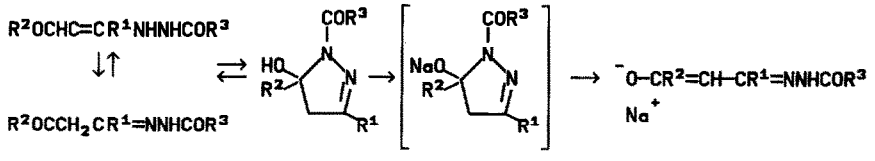
These nitrogen derivatives are of interest from the theoretical point of view for being polydentate they have at least three reactive centres, viz., nitrogen, oxygen and α-carbon atoms. This makes them much more complex objects of investigation than the parent anions of 1,3-dioxo-compounds since the latter undergo electrophilic attack on carbon and oxygen atoms.

Data concerning reactions of neutral forms of nitrogen derivatives of 1,3-dioxo-compounds with electrophiles are

inconsistent.[1] In particular this is true for acylation. It has been reported that in case of imines of 1,3-ketoaldehydes and 1,3-diketones N-acylation is the sole or the preponderant[1-3] process although examples of selective O-[4] or C-acylation[5] are known.

In the present work we report on the preparation and acylation of sodium salts of acylhydrazones of 1,3-dioxo-compounds, which are easily available.[6] For this purpose we used typical aroylacetaldehyde, acetylacetone and aroylacetone acylhydrazones (**1-7**), which are capable of existing as a ring-chain tautomeric mixtures of enehydrazine, hydrazone and 5-hydroxy-2-pyrazoline forms.[6] It should be noted that anions of acetone acylhydrazones are well known and have been used as synthons in some cases.[7]

We have found that on treatment with sodium methoxide or sodium hydroxide, or with sodium metal, acylhydrazones (**1-7**) practically quantitatively yield the respective sodium salts (**8-14**).



1-7 **A** **B** **8-14**

	R^1	R^2	R^3
1, 8	H	C_6H_5	CH_3
2, 9	H	C_6H_5	C_6H_5
3, 10	H	$4\text{-}BrC_6H_4$	C_6H_5
4, 11	CH_3	CH_3	C_6H_5
5, 12	CH_3	C_6H_5	CH_3
6, 13	CH_3	C_6H_5	C_6H_5
7, 14	CH_3	$4\text{-}CH_3OC_6H_4$	C_6H_5

These salts, which may be represented by at least two possible tautomers **A** and **B**, proved to have the structures **B** on the basis of the ^1H and ^{13}C NMR spectra (Tables 1 and 2).

It is noteworthy that, out of a large variety of nitrogen derivatives of 1,3-dioxo-compounds, we found that only acylhydrazones of 1,3-diketones and 1,3-ketoaldehydes formed stable sodium salts. Our efforts to prepare sodium derivatives of dimethylhydrazones, of alkyl- and arylimines of arylamides and esters of acetoacetic acid, of aroylacetaldehydes and of acetylacetone, benzoylacetone in the reactions with sodium hydroxide, with sodium metal, and with sodium methoxide or amide, all failed. Acylhydrazones of acetoacetic

Table 1. The ^1H NMR Data of Na-Salts **8-14** in DMSO-d_6
(HMDS - external standard)

Compound	δ, ppm			
	HCCR[2] (J, Hz)	CH_3, s	$H_{arom.}$, CCHN	NH, br. s
8	5.60 d (10)	2.10	7.40-7.60 m (3H), 7.90-8.10 m (3H)	12.60
9	5.74 d (8)	-	7.40-7.61 m (6H), 7.90-8.10 m (3H), 8.20-8.28 m (2H)	12.50
10	5.54 d (4)	-	7.24-8.10 m (10H)	12.40
11	4.70 s	1.84, 2.06	7.10-7.50 m (3H), 7.88-8.00 m (2H)	12.50
12[a]	5.64 s	1.98, 2.30	7.30-7.40 m, 8.00-8.10 m	14.60
	5.18 s	2.05, 2.10		
13	5.72 s	2.38	7.40-7.60 m (6H), 8.00-8.10 m (2H), 8.20-8.30 m (2H)	10.68
14	5.68 s	2.36	6.94-7.04 m (2H), 7.40-7.50 m (3H), 7.98-8.04 m (2H), 8.20-8.35 m (2H)	10.64

[a]Two forms.

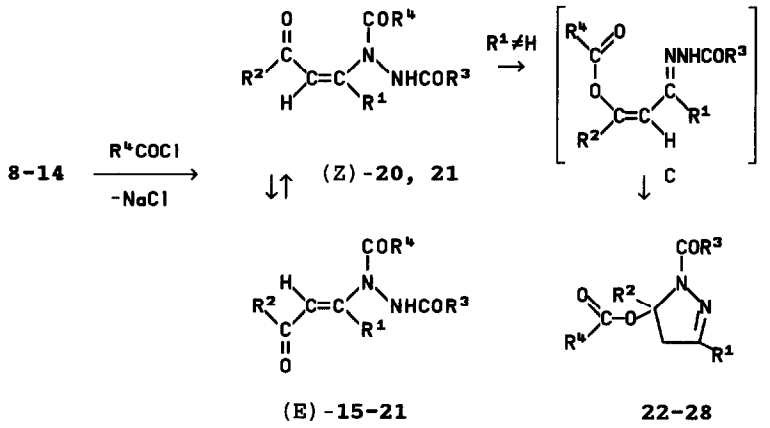
Table 2. The ^{13}C NMR Data of Salts **8-14** in DMSO-d_6

Compound	CH_3	CH	C_{arom}	CN	CON	COR[2]
8	21.6	86.8	126.2, 126.6, 127.6, 143.5	148.9	165.8	177.0
9	-	82.8	127.0, 127.3, 127.9, 129.3, 139.4, 141.2	149.8	161.7	181.9
10	-	85.5	122.6, 125.4, 126.3, 127.6, 131.6, 134.2, 140.8, 141.8	154.8	163.3	180.3
11	18.0, 28.1	90.6	127.0, 127.2, 127.8, 139.9	153.9	162.2	186.1
12[a]	18.0, 22.9	87.6	126.3, 126.5, 127.8, 139.9	153.4	167.3	178.0
	21.8, 25.3	89.5		155.5	164.6	171.5
13	18.2	88.9	126.2, 127.2, 127.9, 128.9, 129.9, 139.6, 141.6	154.7	163.3	179.1
14	18.3, 55.2	87.3	113.0, 127.3, 128.0, 134.4, 140.0, 160.2	154.5	162.9	178.9

[a]Two forms.

acid derivatives also did not yield the desired salts. All these substrates proved to be inert under mild conditions and were completely decomposed on heating.

Acetylation and benzoylation of the sodium derivatives of aroylacetaldehydes (**8-10**) with appropriate acid chlorides yield only the β-ketoenehydrazides (**15-19**), which are stable up to 150 °C.



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
15	H	C_6H_5	CH_3	CH_3	**21, 24**	CH_3	C_6H_5	CH_3	CH_3
16	H	C_6H_5	CH_3	C_6H_5	**23**	CH_3	CH_3	C_6H_5	C_6H_5
17	H	C_6H_5	C_6H_5	CH_3	**25**	CH_3	C_6H_5	CH_3	C_6H_5
18	H	C_6H_5	C_6H_5	C_6H_5	**26**	CH_3	C_6H_5	C_6H_5	CH_3
19	H	4-BrC_6H_4	C_6H_5	CH_3	**27**	CH_3	C_6H_5	C_6H_5	C_6H_5
20, 22	CH_3	CH_3	C_6H_5	CH_3	**28**	CH_3	4-$CH_3OC_6H_4$	C_6H_5	CH_3

In the ^{13}C NMR spectra of these products (Table 3) there are signals for the ketone carbonyl group (189-190 ppm), two amide carbonyl groups (166-173 ppm) and the olefinic carbon atoms (104-105 ppm and 138-142 ppm).

The $^3J_{H-H}$ values for the olefinic protons (13-15 Hz) of the β-ketoenehydrazides (**15-19**) (where R^1 =H) in the ^1H NMR spectra (Table 4) unambiguously prove their (E)-configuration.

Thus in this case N-acylation occurred.

On acylation of the sodium salts of derivatives of 1,3-diketones (**11-14**) (where R^1 = CH_3), the outcome was quite different: the sole products were 1-acyl-5-acyloxy-2-pyrazolines (**22-28**).

The diastereotopy of the protons of the CH_2 groups in the ^1H NMR spectra (Table 5), the presence of the C-5 signals at 97-102 ppm in the ^{13}C NMR spectra ($CDCl_3$) of the 2-pyrazolines (**22-28**) [typical for 5-hydroxy-2-pyrazolines (95-105 ppm)[8,9]], and the presence of the ^{13}C

Table 3. The ^{13}C NMR Data of β-Ketoenehydrazides **15-20** in DMF-d_7

Compound	CH_3	CH	C_{arom}	CN	CON	COR^2
15	20.7, 24.5	104.3	128.6, 129.2, 130.1, 133.6	139.0	169.2, 172.1	189.8
16	20.3	105.0	128.5, 128.8, 129.1, 129.6, 129.8, 131.9 132.1, 133.2	141.5	168.4, 170.3	189.6
17	21.4	104.5	129.2, 129.4, 129.8, 130.0, 130.1, 132.4, 133.2, 133.6	141.4	166.7, 172.8	189.6
18		104.8	128.1, 128.8, 129.2, 129.9, 131.4, 132.0, 132.1, 132.9, 133.2, 133.8, 138.8	138.8	166.7, 170.5	189.6
19	20.9	104.4	128.1, 129.1, 130.0, 131.1, 131.5, 133.0, 133.3, 133.9	139.6	166.1, 172.3	189.8
(E)-**20**[a]	21.3, 22.7, 31.7	120.1	127.0, 128.0, 129.5, 134.2	153.9	166.1, 172.1	197.3

[a] In $CDCl_3$.

Table 4. The Physical Details and ^1H NMR data of β-Ketoenehydrazides **15-20**

Compound (Yield, %)	M.p., [a] °C	δ, ppm [b] HC=CN (J, Hz)	C=C(H)N (J, Hz)	CH_3, s	$H_{arom.}$	NH, br.s
15 (55)	128-129	6.48 d (13)	8.32 d (13)	2.04, 2.10	7.30-7.40 m (3H), 7.70-7.80 m (2H)	12.50
16 (38)	67-68	6.42 d (14)	8.26 d (14)	1.70	7.25-7.75 m (10H)	9.94
17 (42)	oil	6.60 d (13)	8.50 d (13)	2.24	7.30-7.60 m (6H), 7.80-8.08 m (4H)	12.50
18 (51)	155-156	6.82 d (14)	8.60 d (14)	-	7.20-8.10 m (15H)	11.35
19 (38)	186-187	6.72 d (14)	8.60 d (14)	2.24	7.40-8.10 m (9H)	11.50
(E)-**20** (7)	oil	6.44 s	c	2.05, 2.11	7.30-7.50 m (3H), 7.68-7.80 m (2H)	10.30
(Z)-**20** (8)	oil	6.06 q (1)	d	2.10, 2.16	7.30-7.60 m (3H), 7.65-7.80 m (2H)	10.40

[a] **15, 19** - from hexane-benzene (4:1); **16** - from pentane-ether (4:1), **18** - from benzene; [b] **15, 17** - in DMF-d_7, **16, 18-20** - in $CDCl_3$; [c] 2.32 (s, 3H, $CH_3C=C$); [d] 2.31 (d, J=1 Hz, 3H, $CH_3C=C$).

Table 5. The Physical Details and ^1H NMR Data of 1-Acyl-5-acyloxy-2-pyrazolines **22-28**

Compound[a] (Yield, %)	CH_2, AB system[b]	CH_3, s	δ, ppm in $CDCl_3$ $H_{arom.}$
22 (37)	3.18, 3.56	1.76, 2.04, 2.22	7.20-7.45 m (3H), 7.70-7.80 m (2H)
23 (44)	3.21, 3.69	1.79, 1.93	7.35-7.43 m (6H), 7.75-7.85 m (2H), 7.98-8.10 m (2H)
24[c] (35)	3.70, 4.00	1.74, 1.75, 1.94	7.39-7.58 m (3H), 7.85-7.94 m (2H)
25 (40)	3.63, 4.27	1.77, 1.83	7.33-8.33 m (10H)
26 (47)	3.69, 4.12	1.91, 2.20	7.20-7.56 m (6H), 7.66-7.94 m (4H)
27 (39)	3.84, 3.69	1.99	7.30-8.00 m (15H)
28 (37)	3.64, 4.05	1.91, 2.21	6.73-6.82 m (2H), 7.30-7.45 m (3H) 7.61-7.70 m (2H), 7.75-7.94 m (2H)

[a] **22-25, 27** were isolated as oils; **26, 28** were recrystallized from hexane-benzene (5:1) (melting points: 105-106 and 79-80 °C respectively); [b] J=17-18 Hz; [c] In DMF-d_7.

Table 6. The ^{13}C NMR Data of 1-Acyl-5-acyloxy-2-pyrazolines **22-28**

Compound	CH_3	C-4	C-5	$C_{arom.}$	C-3	CON	COO
22	22.0, 24.1, 31.0	47.3	97.9	125.1, 126.9, 128.2, 132.1	152.9	166.1	202.2
23	24.3, 31.7	48.3	99.6	126.9, 127.6, 128.5, 129.7, 131.0, 131.4, 132.4, 134.1	154.5	164.6	203.1
24	11.2, 21.9, 24.6	43.5	98.4	127.4, 128.0, 129.2, 133.2	154.6	171.2	195.5
25	11.3, 24.8	43.6	100.1	127.6, 128.2, 128.6, 129.3, 129.5, 130.2, 130.8, 133.3	156.2	171.3	195.5
26	22.3, 25.1	44.2	99.4	127.2, 128.6, 128.8, 129.5, 130.5, 131.6, 133.4, 137.9	154.4	167.6	195.7
27	24.8	43.6	100.1	127.6, 127.8, 128.0, 128.2, 128.5, 128.6, 128.7, 129.7, 130.0, 131.0, 131.4, 133.3	154.9	170.3	195.3
28	22.0, 24.6, 55.3	43.2	99.2	113.6, 124.6, 126.7, 128.3, 130.4, 130.8, 131.1, 163.5	154.0	167.3	193.6

signals of the ester (193-203 ppm) and amide groups (164-171 ppm) (Table 6), prove the structures (**22-28**) proposed.

In the ^{17}O NMR spectrum of **22** the signal at 175.0 ppm corresponds to the O_{sp^3} atom while the signals at 370.0 ppm and at 390.0 ppm confirm the presence of the amide and of the ester oxygen carbonyl atoms.[10]

Further evidence for the structure of **22** was provided by its direct synthesis by treating 5-hydroxy-2-pyrazoline **4** with acetic anhydride.

It plausible that the 2-pyrazolines (**22-28**) are the products of direct O-acylation of the tautomeric form B of the sodium derivatives (**11-14**). However investigation of the acylation of the sodium salts **11** and **12** under mild conditions (-30 ^0C) showed that this is not the case. Under these conditions acylation yielded compounds **20** and **21** which did not have the 1-acyl-5-acyloxy-2-pyrazoline structures, and thus could be the linear products of N-, O- or C-acylation.

In the ^{15}N NMR spectrum of **21** (Table 7) there were two signals of N_{sp^3} atoms, viz., a doublet at 116.8 ppm (J=102 Hz) and a singlet at 132 ppm assigned to nitrogen atoms of the amide groups.[11] In the ^{17}O NMR spectrum there were three O_{sp^2} signals. The low field signal was assigned to the ketone group and the other two signals could be referred to the amide groups.[10]

In the ^1H NMR spectrum of **21**, along with the other signals there was a doublet at 2.33 ppm (J=0.8 Hz, CH_3C=CH) and an olefinic quartet at 7.24 ppm with the same coupling constant. In the ^{13}C NMR spectrum the latter signal was associated with the =CH doublet at 113.2 ppm (Table 7). A second olefinic carbon appeared at 154.7 ppm.

These data established the presence of a CH_3C=CH fragment. The signal at lowest field (191.0 ppm) in the ^{13}C NMR spectrum was assigned to the C_6H_5COCH= carbonyl group; in ^{13}C $\{^1H\}$ selective decoupling experiments it was resolved into a triplet (J=6 Hz) and into a doublet (J=6 Hz) on irradiation of the olefinic proton and the ortho-protons of the aromatic ring respectively.

The ^1H and ^{13}C NMR spectra of **20** showed signals similar to those of **21** (Tables 3 and 4).

So, the spectral data obtained unambiguously proved β-ketoenehydazide structures of **20** and **21**.

Thus N-acylation took place in this case also.

Table 7. NMR Data (in acetone-d_6) and Yields of Compounds (E)-**21** and (Z)-**21**

	(E)- **21**[a]	(Z)-**21**[a]
^1H	1.98 (s, 3H, CH_3CON);	1.80 (s, 3H, CH_3CON);
	2.05 (s, 3H, CH_3CON);	1.88 (s, 3H, CH_3CON);
	2.33 (d, J=0.8 Hz, 3H, $CH_3C=C$);	2.24 (d, J=1 Hz, 3H, $CH_3C=C$);
	7.24 (q, J=0.8 Hz, 1H, CH);	6.76 (q, J=1 Hz, 1H, CH);
	7.32-7.38 (m, 3H, Ph);	7.36-7.40 (m,3H, Ph);
	7.80-7.88 (m, 2H, Ph);	7.82-7.92 (m, 2H, Ph);
	9.95 (br. s, 1H, NH)	9.60 (br. s, 1H, NH)
^{13}C	17.1, 20.4, 22.8 (CH_3);	20.4, 21.1, 22.1 (CH_3);
	113.2 (CH); 127.9, 128.7,	117.8 (CH); 128.8, 129.2,
	132.6, 139.8 (Ph);	133.4, 139.0 (Ph);
	154.7 (=C-N);	153.7 (=C-N);
	169.1, 172.1 (CON);	169.5, 171.2 (CON);
	191.0 (COPh)	189.2 (COPh)
^{17}O	350.8, 390.8 (CON);	352.1, 373.6 (CON);
	529.2 (COPh)	523.2 (COPh)
^{15}N[b,c]	116.8 (d, J=102 Hz, CONH);	120.3 (d, J=100 Hz, CONH);
	132.3 (CON)	159.7 (CON)
Yield, %	15	10

[a]Both isomers melt in the 60-80 °C range with isomerization.
[b]$Cr(acac)_3$ (0.05 g) was added.
[c]The assignments were confirmed by the INEPT NMR spectrum.

NMR spectral investigation showed that on monitoring at room temperature **21** underwent reversible isomerization. In the ^1H, ^{13}C, ^{15}N and ^{17}O NMR spectra of the isomerization product isolated in a pure state there was practically the same set of signals as in the spectra of its precursor but with only small differences of chemical shifts (Table 7). This indicates that the change is simply a stereoisomerization of **21**.

The β-ketoenehydrazide **20** quantitatively underwent similar

stereoisomerization. In the ^1H NMR spectrum of the steroisomer (Table 4) there was a quartet at 6.06 ppm coupled to a doublet at 2.32 ppm with the same J constant responsible for spin-spin coupling in the $CH_3C=CH$ fragment. The comparison of this spectrum with that of the initial β-ketoenehydrazide in which these signals were singlets pointed to the (E)-configuration of the primary product of N-acylation and the (Z)-configuration of its stereoisomer.

In case of **21** the (E)-configuration could be assigned to the initially formed isomer with the lower field olefinic proton signal, by analogy with the isomer of **20** (Tables 4 and 7) while the (Z)-configuration could be assigned to its isomerization product.

On keeping for a longer time the (Z)-isomers of **20** and **21** yielded 1-acyl-5-acyloxy-2-pyrazolines **22** and **24** respectively (the process was monitored by NMR spectroscopy).

Similar transformations were observed in case of acylation of the salts **13** and **14** in mild conditions, as shown by TLC and NMR spectral investigation of the reaction. The corresponding intermediate β-ketoenehydrazides were not isolated in a pure state.

Thus, the transformations observed can be summarized as follows: acylation of sodium salts of 1,3-diketone acylhydrazones primarily yields (E)-β-ketoenehydrazides, the latter undergoing subsequent stereoisomerization to the respective (Z)-isomers followed by isomerization to unstable intermediates **C** as a result of a 1,5-N,O-acylotropic shift, and finally their isomerization to the 1-acyl-5-acyloxy-2-pyrazolines (**22-28**).

The initial generation of (E)-isomers and the subsequent E→Z stereoisomerization of the acylation products are typical for alkaline salts of 1,3-diketones.[12] Furthermore, a 1,5-O,O-acylotropic shift is a well known property of O-acyl derivatives of 1,3-diketones while 1,5-N,N-acylotropy is typical for N-acyl derivatives of diimines of 1,3-diketones.[13]

As to acylation of sodium derivatives of acylhydrazones of aroylacetaldehydes, the process goes no further than the first stage, probably because of the thermodynamic stability of the (E)-β-ketoenehydrazides (**15-19**).

Thus we show that sodium salts (**8-14**) undergo primarily only N-acylation over a broad temperature range (-30 - 30 °C). However, depending on the nature of the parent 1,3-dioxo-compounds, this reaction can be used for the preparation of various linear and cyclic substances previously unknown, such as β-ketoenehydrazides and 1-acyl-5-acyloxy-2-pyrazolines.

Experimental

The ^{1}H NMR (100 MHz) and ^{13}C NMR (20.41 MHz) spectra were recorded with a Tesla-BS-497 spectrometer using HMDS as an internal standard (unless otherwise stated). The ^{17}O NMR (67.8 MHz) and ^{15}N NMR (50.68 MHz) spectra were recorded with a Bruker AM-500 spectrometer, chemical shifts were measured against D_2O and CH_3NO_2 respectively, the NH_3-scale was used in the latter case. The melting points were determined in capillaries and are uncorrected. Preparative TLC and column chromatography were performed using silica gel Chemapol L 40/100 with benzene-CCl_4-acetone (2:4:1). The purity of the compounds was checked by TLC using Silufol-UV-254 plates. The elemental analysis data (C, H, N) of the new compounds agreed with calculated values to within 0.2%. Solvents were dried by standard methods.

1-Acyl-5-hydroxy-2-pyrazolines (**1-7**).
1-Acetyl-5-hydroxy-5-phenyl-2-pyrazoline (**1**),[14] 1-benzoyl-5-hydroxy-5-phenyl-2-pyrazoline (**2**),[15] 1-benzoyl-5-(4-bromophenyl)-5-hydroxy-2-pyrazoline (**3**),[16] 1-benzoyl-3,5-dimethyl-5-hydroxy-2-pyrazoline (**4**),[17] 1-acetyl-5-hydroxy-3-methyl-5-phenyl-2-pyrazoline (**5**),[14] 1-benzoyl-5-hydroxy-3-methyl-5-phenyl-2-pyrazoline (**6**)[18] and 1-benzoyl-5-hydroxy-5-(4-methoxyphenyl)-3-methyl-2-pyrazoline (**7**)[18] were prepared following published procedures.

Sodium salts of acylhydrazones of 1,3-dioxo-compounds (**8-14**).
Method A. To a solution of 1-acyl-5-hydroxy-2-pyrazolines (**1-7**) (50 mmol) in methanol (100 ml) was added sodium methoxide (45 mmol) in methanol (100 ml). The solution was evaporated under reduced pressure and the residue was washed with 50 ml of ether three times, dried and yielded a brown solid, melting above 250 °C.
Method B. A similar procedure was carried out using sodium hydroxide (45 mmol) in water (30 ml) instead of sodium methoxide in methanol.
Method C. To a stirred suspension of sodium metal (45 mmol) in dry ether (100 ml) was added a solution of 1-acyl-5-hydroxy-2-pyrazolines (**1-7**) (50 mmol) in dry ether (100 ml) dropwise at 0 °C. After the addition the mixture was heated to room temperature and stirred for 2 h. The resulting salt was filtered off and purified as described in Method A.

Our attempts to apply Methods A, B and C to the other nitrogen derivatives (mentioned in the text after the first scheme) were unsuccessful (reactions with sodium amide were carried out as described for sodium metal in Method A).

1-Aryl-3-(1,2-diacylhydrazino)prop-2-en-1-ones (**15-19**).
To a suspension of the sodium salts (**8-10**) (5 mmol) in dry acetonitrile (30 ml) was added an appropriate acid chloride (5 mmol) in one portion at 0 °C. After stirring for 2 h at this temperature the mixture was filtered to remove sodium chloride and the solution was evaporated. The residue was purified by recrystallization or column chromatography.

1-Acyl-5-acyloxy-5-aryl(methyl)-3-methyl-2-pyrazolines (**22-28**).
The reaction and purification were done under identical conditions using the sodium salts (**11-14**).

5-Acetyloxy-1-benzoyl-3,5-dimethyl-2-pyrazoline (**22**).
To a solution of **4** (1.77 g, 37.5 mmol) in CH_2Cl_2 (30 ml) were added acetic anhydride (9 ml) and pyridine (3 ml). The mixture was kept at room temperature for 5 h. The excess reagents were removed *in vacuo* and the residue was chromatographed on a silica gel column yielding 1.15 g (35%) of **22**.

4-(1-Acetyl-2-benzoylhydrazino)pent-3-en-2-one [(E)-**20** and (Z)-**20**].
To a suspension of the sodium salt (**11**) (3g, 12.5 mmol) in dry acetonitrile (60 ml) was added acetyl chloride (0.9 ml, 12.5 mmol) dropwise over a period of 15 min at -35 °C. After stirring for 1 h at -25 °C the mixture was filtered to remove sodium chloride. The solution was evaporated *in vacuo* and the residue was subjected to preparative TLC to afford (E)-**20** and (Z)-**20**.

1-Phenyl-3-(1,2-diacetylhydrazino)but-2-en-1-one [(E)-**21** and (Z)-**21**].
The above procedure was performed starting with the sodium salt (**12**) and acetyl chloride.

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