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REACTION OF SUBSTITUTED HYDRAZONES WITH BASES. SYNTHESIS OF α-AMINODIALKYLDIAZENES

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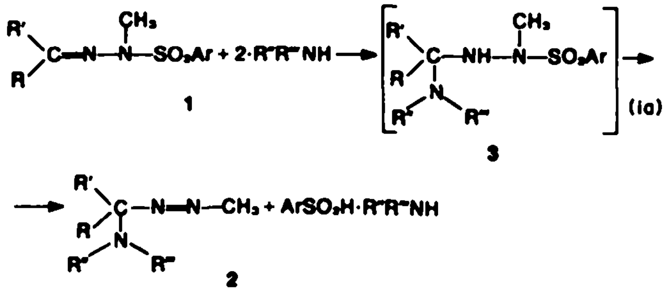
Abstract—A reaction of N,N-disubstituted hydrazones (1) with bases has been investigated. N - Methyl - N - tosylhydrazones of aliphatic carbonyl compounds have been shown to combine with primary and some secondary aliphatic amines to form α-aminodialkyldiazenes (2) hitherto unknown, and with triethylamine and alcoholic solutions of alkalies to form symmetric azines (10). Some structural factors contributing to the formation of 2 have been elucidated.

The interaction of aryl sulphonyl hydrazones of various carbonyl compounds with bases has been widely investigated and is of great preparative value.[1-4] It should be noted, however, that all these reactions were carried out with hydrazones containing an H-atom bonded to a N atom and are based on the ability of the H atom to be ionized in the presence of bases. This paper deals with a study of behavior of bases in respect of hydrazones not containing an H atom bonded to a N atom. The hydrazones investigated by us are listed in the Table 1.

Methylidene-, ethylidene- and isobutylidene - N methyl - N - tosylhydrazones (1a–c) combining with primary aliphatic amines under mild conditions turned out to form α-aminodialkyldiazenes (2)[7] unknown heretofore (eqn 1a).

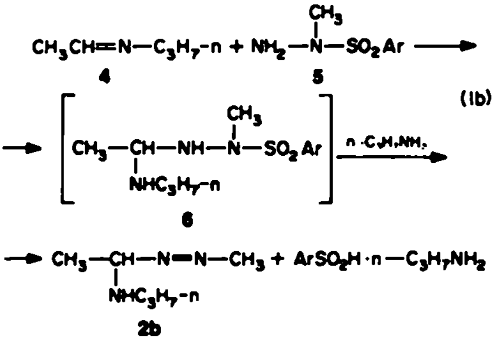


R—R'—R''—R''' = H, Alk; Ar—$C_6H_4CH_3$

Table 1. The hydrazones investigated in this paper

		$R' \rangle C=N-N \langle Y$ $R \qquad 1 \qquad X$		
1	R	R'	X	Y
1a	H	H	CH_3	$SO_2C_6H_4CH_3$
1b	CH_3	-"-	-"-	- " -
1c	$\begin{matrix}CH_3\\CH_3\end{matrix}\rangle CH$	-"-	-"-	- " -
1d	C_6H_5	-"-	-"-	- " -
1e	CH_3	CH_3	-"-	- " -
1f	$(-CH_2-)_5$		-"-	- " -
1g	CH_3	H	-"-	$COOCH_3$
1h	-"-	-"-	-"-	$COOC_6H_5$
1i	-"-	-"-	C_6H_5	$SO_2C_6H_4CH_3$
1j	-"-	-"-	-"-	$COOCH_3$
1k	-"-	-"-	-"-	$COOC_6H_5$

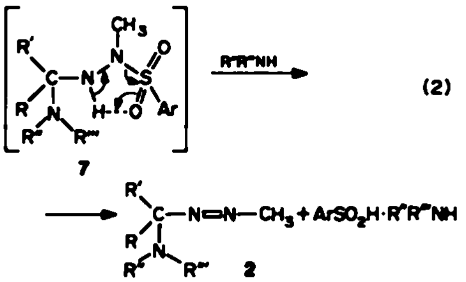
The reaction seems to be a combination of two known reactions: the addition of a NH group to C=N bond[8-10] and the formation of azo compounds from N - alkyl - N - arylsulphonylhydrazones.[11] A probable intermediate seems to be α-aminohydrazide (3). The possibility of formation of 3 is supported by synthesis of α - N - propylaminoethylmethyldiazene (2b) through the interaction between N - ethylidene - n - propylamine (4) and N - methyl - N - tosylhydrazide (5) which should proceed through the formation of 6 (eqn 1b).



(Ib)

Ar=$C_6H_4CH_3$

The ensuing decomposition of 3 may take place both by ionization of the H atom bonded to the N atom under action of excess amine and through a cyclic 5-membered transition state (eqn 2).



(2)

Sulphinic acid is liberated in both cases. The liberation of sulphinic acid is generally specific of a sulphonylhydrazine fragment and occurs most commonly in those cases when a proton appears at a N atom located in β-position to the S atom.[11,12]

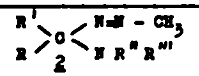
The α-aminodialkyldiazenes 2 and their yields depending on the reaction conditions are presented in Table 2.

Stretching vibrations of the NH group (3320 cm^{-1}) and the N=N group (1450 cm^{-1}) are visible in IR spectra of diazenes 2. A distinct intensive band of the N=N group (1440 cm^{-1}) is seen in a Raman spectrum.

The proton chemical shift of the CH_3–N=N group in the ^{1}H NMR spectrum is 3.6–3.8 ppm. This value is close to that of the same group (3.89) in α-hydroxydialkyldiazenes obtained recently.[13] The absence of a signal of sp^2-hybridized C atom in ^{13}C NMR spectrum discards alternative hydrazone and amidrazone structures. The chemical shifts and multiplicity (off resonance) of signals in ^{13}C NMR spectra reveal the presence of $CH_3CH{<}^{N}_{N}$ (19, 6q; 84, 6d), =N–CH_3 (55, 4q), N–$CH_2CH_2CH_3$ (47, 5t; 22, 3t; 11, 3q) fragments in compound 2b and N–$CH_2CH_2CH_2CH_3$ (45, 3t; 32, 4t; 20, 1t; 13, 6q), =N–CH_3 (55, 2q), $(CH_3)_2CH$–$CH{<}^{N}_{N}$ (16, 8q; 17, 2q; 31, 59d; 93, 4d) in α - n - butylamino - β - methylpropylmethyldiazene (2d), which agrees fully with the structure proposed. The resonance signal of a methine C atom bonded to two N atoms in the compound 2d is shifted by 8.8 ppm to a low field as compared with the same atom in the compound 2b owing to the β-effect of the Me group in the isopropenyl residue. In accordance with the structure proposed the presence of an asymmetric centre in molecule 2d gives rise to a magnetic nonequivalence of the Me C atoms in the isopropenyl residue.

In spite of the fact that yields of diazenes 2 do not exceed 60% (Table 2) the amount of sulphinic acid formed was not less than 90–95%. Other reaction

Table 2. α-Aminodialkyldiazenes 2



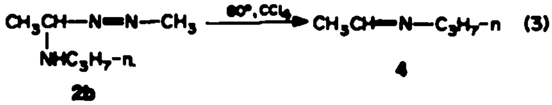
2	R	R'	R''	R'''	Time (day)	Solvent	Yield,%
2a	H	H	H	n-C_3H_7	4	THF	38,1
2b	CH_3	-"-	-"-	-"-	6	-"-	44,7
-"-	-"-	-"-	-"-	-"-	6	CH_2Cl_2	40,6
2c	$(CH_3)_2CH$	-"-	-"-	CH_3	7[*)]	-"-	51,0
2d	-"-	-"-	-"-	n-C_4H_9	7	ether	36,0
-"-	-"-	-"-	-"-	-"-	8	water	42,0
2e	-"-	-"-	-"-	$CH_2CH=CH_2$	15	ether	51,0
2f	-"-	-"-	-"-	H	10[**)]	CH_2Cl_2	50,0
2g	-"-	-"-	$(-CH_2-)_5$		30	ether	61,0
2h	$(-CH_2-)_5$		H	n-C_3H_7	15	ether	54,0

*) 5°C

**) 9 atm.

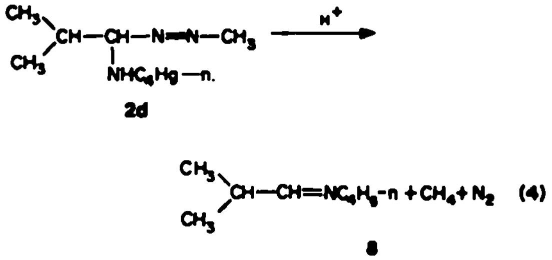
products in all cases were shown to be Schiff's bases (composed by an amine employed in the reaction and a carbonyl hydrazone component) or their trimerization products (reaction 1c with ammonia). The reaction carried out at an elevated temperature (60°) leads to the formation of Schiff's bases mainly and to that of a small amount of diazenes.

The appearance of Schiff's bases can be accounted for either by the instability of diazenes 2 under reaction conditions or by alternative reaction courses. During the investigation of the properties of diazenes 2, it appeared that the thermal stability was not high. Thus, the boiling of the diazene 2b solution in CCl_4 for 15 hr yielded a considerable amount of a Schiff's base (4) (eqn 3).



$$CH_3\underset{\underset{\textbf{2b}}{NHC_3H_7\text{-}n}}{CH}-N{=}N-CH_3 \xrightarrow{80°,\,CCl_4} \underset{\textbf{4}}{CH_3CH{=}N-C_3H_7\text{-}n} \quad (3)$$

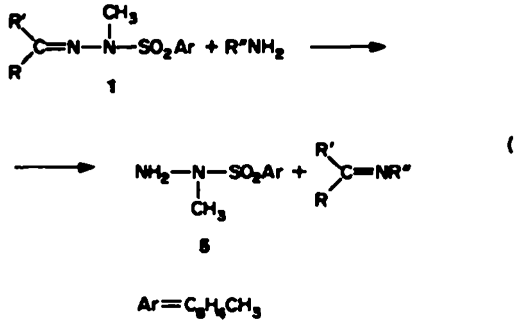
The decomposition of 2 was accelerated considerably in the presence of mineral acids. N - Isobuthyliden - n - buthylamine (8), nitrogen and methane (the latter ones identified by mass-spectrometry) were isolated after a solution of 2d in CH_2Cl_2 with an equimolar amount of hydrochloric acid had been kept for 15 hr (eqn 4). The decomposition of 2d took place similarly in the presence of *p*-toluenesulphinic acid.



(4)

Since sulphinic acid was always present in the mixture during the synthesis of 2, the appearance of a Schiff base could be accounted for by an acid-catalyzed decomposition of 2. However, a transamination side reaction was not excluded also (eqn 5). The ability of hydrazide 5 to readily give off sulphinic acid, nitrogen and methane in the presence of bases is known.[14]

The behavior of diazenes 2 in the presence of acids is similar to that of α-hydroxyalkyldiazenes which form a carbonyl compound and monoalkyldiazenes (9) under these conditions.[15] Therefore diazenes 2 prepared may serve as sources of 9, the chemistry of which has been developing rapidly in recent years.[16]

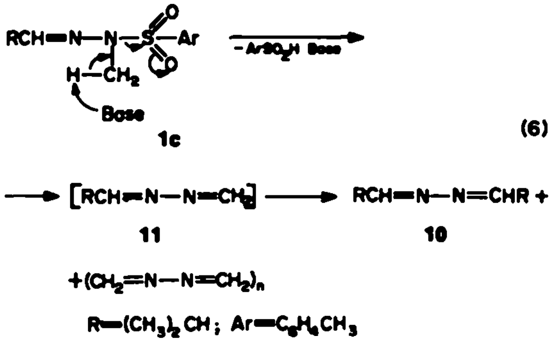


(5)

The simple method found for the preparation of α-aminodialkyldiazenes 2 hitherto unknown from readily available products under mild conditions demonstrates that the synthetic potentialities of substituted hydrazones is far from exhausted. In order to elucidate the structural features of compounds contributing to the formation of 2 as well as to ascertain the possibility of synthesis of other α-substituted diazenes according to this scheme, we examined the behavior of N - methyl - N - tosylhydrazones of aldehydes (by example of 1c) in respect of amines of another type and of other nucleophilic reagents.

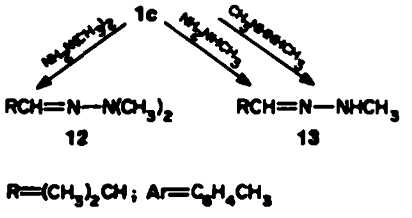
Primary amines containing an aryl or a branched alkyl residue, failed to react with 1c during 20 days. A negative result was also obtained with diethylamine. However, a decrease of steric hinderance near the N atom of secondary amines allows the reaction to proceed along its appropriate course. The interaction of hydrazone 1c with piperidine brought about the formation of α - N - piperidino - β - methylpropylmethyldiazene (2g, yield 61%).

A symmetric aldazine (10) turned out unexpectedly to be formed (though in low yield yet) when the hydrazone 1c was kept at 20° for a long while or heated with triethylamine or alcoholic alkali. As a possible explanation for the formation of 10, one may suppose that the first stage is the attack on Me hydrogen by a base leading to the formation of a non-symmetric azine (11) which subsequently undergoes a symmetrization (eqn 6). The ability of the nonsymmetrical azines to undergo a symmetrization is well known.[17]



(6)

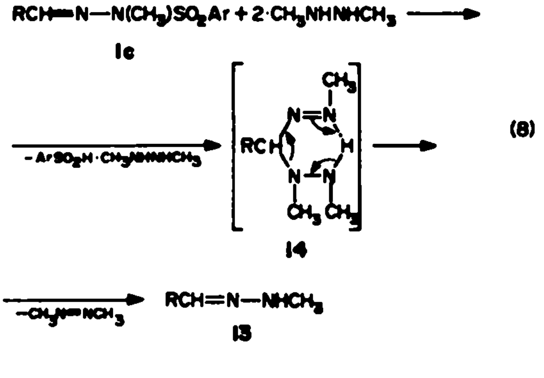
Hydrazones 12 and 13 along with sulphinic acid were obtained in the course of reaction of 1c with hydrazines at various degrees of alkyl substitution (eqn 7).



(7)

The formation of hydrazones 12 and 13 in the course of reaction of 1c with monomethylhydrazine and nonsymmetric dimethylhydrazine could be accounted for by the transhydrazonation characteristic of hydrazones.[18,19]

However, transhydrazonation does not allow one to explain the outcome of the reaction with symmetric dimethylhydrazine (the formation of 13). Most probably this is due to the formation of *α*-hydrazinodialkyldiazene (14), which appears to be instable and seems to decompose in accordance with eqn (8).



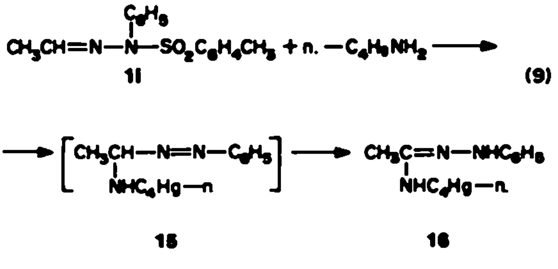
$R{=}(CH_3)_2CH$; $Ar{=}C_6H_4CH_3$

We do not exclude such a manner of formation of hydrazones 12 and 13 in the case of interaction of 1e with two other hydrazones.

Apart from the interaction between 1e and various nucleophilic reagents we have studied the behavior of hydrazones of various structures in respect of primary aliphatic amines (by example of *n*-propylamine). It turned out that the substitution of an aliphatic for an aromatic aldehyde residue in the carbonyl part of the hydrazone (benzylidene - N - methyl - N - tosylhydrazone 1d) caused the reaction with *n*-propylamine to stop completely at 20°, whereas at 60° N-benzylidenepropylamine was formed.

The substitution of an aldehyde for a ketone residue in the carbonyl part of the hydrazone resulted in the formation of *α*-aminodialkyldiazenes, but they are not stable. Only *α* - *n* - propylaminocyclohexylmethyldiazene (2h), obtained from cyclohexyliden - N - methyl - N - tosylhydrazone (1f), could be identified.

The hydrazone (1i) reacts with primary aliphatic amines probably in the same way as hydrazones 1a–c, but *α*-aminoalkylphenyldiazene (15) after formation, re-arranged into amidrazone (16) which was finally isolated (eqn 9).

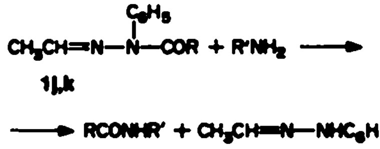


$$CH_3CH{=}N{-}\underset{\mathbf{1i}}{\overset{C_6H_5}{N}}{-}SO_2C_6H_4CH_3 + n.{-}C_4H_9NH_2 \longrightarrow \left[\underset{\mathbf{15}}{CH_3\underset{NHC_4H_9-n}{CH}{-}N{=}N{-}C_6H_5}\right] \longrightarrow \underset{\mathbf{16}}{CH_3\underset{NHC_4H_9-n}{C}{=}N{-}NHC_6H_5} \qquad (9)$$

The ease of formation of amidrazone 16 is supported by the ability known of arylalkyldiazenes to re-arrange readily into hydrazones.[20]

The replacement of the arylsulphonyl group by the acyl in the hydrazones changes their reactivity sharply. After treating the hydrazones (1g and 1h) with *n*-propylamine, both compounds returned unchanged.

The replacement of the Me group by the phenyl in these hydrazones (1j and 1k) does not allow the amine to link to the C=N bond; instead the amine attacks the CO group to form corresponding amides (eqn 10).



$$\underset{\mathbf{1j,k}}{CH_3CH{=}N{-}\overset{C_6H_5}{N}{-}COR} + R'NH_2 \longrightarrow RCONHR' + CH_3CH{=}N{-}NHC_6H_5$$

1j: $R{=}CH_3$; (10)
1k: $R{=}C_6H_5$; $R'{=}C_4H_9{-}n$.

EXPERIMENTAL

IR spectra were recorded in films between NaCl crystals with UR-10. ^1H NMR spectra were measured in CCl_4 with the Perkin–Elmer Model R-12 (spectrometer frequency 60 M c/s) with HMDS as an internal standard. The chemical shifts are given in the *δ* (ppm) scale. ^{13}C NMR spectra were obtained using JNM-PS-100. Mass spectra were taken with a CH-6 Varian Mat.

General method of preparation of α-aminodialkyldiazenes 2. A mixture of 0.1 mole of N - tosyl - N - methylhydrazone of a carbonyl compound and 0.2 mole of amine (or ammonia) in 40–50 ml of an appropriate solvent was kept at 20° for to 4–30 days (Table 2). The ppt of the amine salt and sulphinic acid was filtered off, or else the mixture was washed with water, the organic layer was separated, dried with K_2CO_3, the solvent was distilled off under atmospheric pressure, the residue was distilled in vacuum.

The physical properties of the diazenes obtained are given in Table 3.

Preparation of the hydrazones 1a–f. 0.12 mole of a carbonyl compound were added dropwise to a soln of 0.1 mole of N-tosyl-N-methylhydrazine (obtained according to ref. 11) in 50 ml of alcohol (MeOH, EtOH, PrOH) at 0°. The mixture was stirred for 1 hr at this temp, and for 2–10 hr at 20°. The hydrazone obtained was filtered off and crystallized from an appropriate solvent. The physical properties of hydrazones 1a–f thus prepared are shown in the Table 4.

Ethyliden - N - methyl - N - acetylhydrazone 1g. A mixture of 0.12 mole of acetaldehyde and 0.1 mole of N - methyl - N - acetylhydrazine[21] in 50 ml EtOH was kept at 0° for 15 hr. After the solvent was removed and the residue was distilled in vacuum, 5.4 g (47%) of 1g with b.p. 37–40°/1 mm was obtained; n_D^{20} 1.4800. (Calcd: C, 52.60; H, 8.81; N, 24.55; $C_5H_{10}N_2O$; Found: C, 52.48; H, 8.90; N, 24.32%). ^1H NMR: 1.9 (3H, d); 2.15 (3H, s); 3.08 (3H, s); 7.1 (1H, q).

Ethylidene - N - methyl - N - benzoylhydrazone 1h. 6.6 g (0.15 mole) of acetaldehyde and several drops of AcOH were added dropwise to 15 g (0.1 mole) of N - methyl - N - benzoylhydrazine[22] in 50 ml EtOH at 0°. The mixture was stirred at this temp for 1 hr and left to stand in a refrigerator for one night. The ppt was filtered off, washed with cold alcohol yielding 7.1 g (40%) of 1h, m.p. 82–83° from EtOH. (Calcd: C, 68.28; H, 6.85; N, 15.91. $C_{10}H_{12}N_2O$; Found: C, 68.35; H, 6.49; N, 15.56%). ^1H NMR: 1.4 (3H, d); 2.85 (3H, s, N–CH_3); 6.65 (1H, q); 7.03 (5H, m).

Ethylidene - N - phenyl - N - tosylhydrazone 1i. 19 g (0.1 mole) of *p*-toluenesulphochloride was added to a mixture of 13.4 g (0.1 mole) of acetaldehyde phenylhydrazone[23] and 8.4 g (0.1 mole) of pyridine in 100 ml CH_2Cl_2 at 20°. The mixture was stirred for 8 hr at this temp. Then 20 ml of water were added, the organic layer was separated and dried with $MgSO_4$, the solvent was distilled off. This gave 13.8 g (48%) of 1i, m.p. 108–110° from CCl_4. (Calcd: C, 62.50; H, 5.58; N, 9.73; S, 11.12. $C_{15}H_{16}N_2O_2S$: Found: C, 62.22; H, 5.60; N, 9.93; S, 11.25%). ^1H NMR: 1.8 (3H, d); 2.35 (3H, s); 6.93 (1H, q, CH=N); 7.37 (9H, m, Ph,

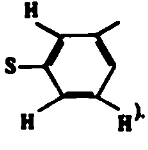


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Table 3. Properties of α-aminodialkyldiazenes 2

No.	B.p. °C/mm	n_D^{20}	Empiric formula mol. weight	Analyt. data calc./found C	H	N	¹H-NMR - spectra
2a	58-60/54	1,4303	$C_5H_{13}N_3$ 115,18	52,14 52,00	11,37 11,04	36,57 36,45	0,85(3H,t); 1,3(2H,m); 1,8(1H,s); 2,4(2H,t); 3,6(3H,s, =N-CH$_3$); 4,2(2H,s, N-CH$_2$-N)
2b[a]	52-53/30	1,4267	$C_6H_{15}N_3$ 129,20	55,77 56,29	11,70 11,64	32,52 32,92	0,87(3H,t); 1,2(3H,d); 1,5(3H,m); 2,37(2H,m); 3,66(3H,s, =N-CH$_3$); 3,95(1H,q, N-CH-N)
2c	47-48/29	1,4294	$C_6H_{15}N_3$ 129,20	55,77 55,47	11,70 11,36	32,52 32,72	0,87(6H,t); 1,9(2H,m); 2,2(3H,s); 3,3(1H,d, N-CH-N); 3,62(3H,s, =N-CH$_3$)
2d	52-53/11	1,4312	$C_9H_{21}N_3$ 171,28	63,11 63,37	12,36 12,14	24,53 24,90	0,85(9H,t); 1,25(4H,m); 1,75(2H,m); 2,25(2H,q); 3,45(1H,d, N-CH-N); 3,65(3H,s, =N-CH$_3$)
2e	54-55/11	1,4437	$C_8H_{17}N_3$ 155,24	61,89 61,67	11,04 11,08	27,07 27,06	0,9(6H,t); 1,95(2H,m); 2,95(2H,t); 3,55(1H,d,N-CH-N); 3,7(3H,s, =N-CH$_3$); 5,05(2H,t); 5,75(1H,m)
2f	41-42/15	1,4335	$C_5H_{13}N_3$ 115,18	52,14 52,36	11,37 11,45	36,57 36,35	1,15(3H,d); 1,28(3H,d); 2,45(2H,s,NH$_2$); 2,9(1H,m); 3,65(3H,s, =N-CH$_3$); 3,95(1H,d, N-CH-N)
2g	101-103/24	1,4595	$C_{10}H_{21}N_3$ 183,29	65,52 65,98	11,55 11,26	22,92 22,90	0,55(3H,d); 0,95(3H,d); 1,41(6H,s); 2,56(5H,m); 3,08(1H,d, N-CH-N); 3,65(3H,s, =N-CH$_3$)
2h	44-45/0,5	1,4690	$C_{10}H_{21}N_3$ 183,29	65,52 65,60	11,55 11,41	22,92 22,62	0,88(3H,t); 1,3(2H,m); 1,5(10H,s); 2,2 (3H,t); 3,58(3H,s, =N-CH$_3$)

[a] Phenylisocyanate derivative of 2b, m.p. 54° (pentane)

Table 4. Properties of the hydrazones 1a-f

No.	M.p., °C	Yield %	Empiric formula, mol.weight	Analytical data calc./found C	H	N	S	¹H - NMR - spectra
1a	109-111 (CCl$_4$)	75	$C_9H_{12}N_2O_2S$ 212,27	50,92 51,15	5,70 5,64	13,20 13,17	15,11 15,30	2,38 (3H,s); 3,05 (3H,s, N-CH$_3$) 6,48 (2H,s, CH$_2$=N); 7,50 (4H,q)
1b	103-104 (CCl$_4$)	88,5	$C_{10}H_{14}N_2O_2S$ 226,294	52,99 53,05	6,23 6,40	12,38 12,52	14,13 14,26	1,9(3H,d); 2,38(3H,s); 2,95(3H,s,N-CH$_3$) 7,1 (1H,q, CH=N); 7,5 (4H,q)
1c	59-60 (hexane)	94	$C_{12}H_{18}N_2O_2S$ 254,346	56,66 56,80	7,13 7,18	11,02 11,03	12,61 12,80	1,0 (6H,d); 2,35(4H,s broad); 2,95 (3H,s, N-CH$_3$); 7,05(1H,d, CH=N); 7,45 (4H,q)
1d	102-103 (CCl$_4$)	80,5	$C_{15}H_{16}N_2O_2S$ 288,36	62,47 62,13	5,60 5,52	9,72 9,86	11,12 11,55	2,3(3H,s); 3,25(3H,s, N-CH$_3$); 7,42(10H,m, CH=N, Ph, S - )
1e	59-61 (hexane)	81	$C_{11}H_{16}N_2O_2S$ 240,320	54,97 54,65	6,71 6,42	11,65 11,78	13,34 13,61	2,05(6H,d); 2,4(3H,s); 2,55 (3H,s, N-CH$_3$); 7,4 (4H,q)
1f	64-65 (ethanol)	79	$C_{14}H_{20}N_2O_2S$ 280,386	59,95 59,67	7,17 7,28	9,97 9,83	11,42 11,75	1,65 (6H,s); 2,25(4H,m); 2,4 (3H,s); 2,6 (3H,s, N-CH$_3$); 7,48 (4H,q)

iso-Butyroaldazine **10**. (1) 25.4 g (0.1 mole) of the N - tosyl - N methylhydrazone of **1c** was boiled with a soln of 4 g (0.1 mole) of NaOH in 100 ml MeOH for 6 hr. The MeOH was distilled off, 50 ml of ether were added, the ppt was filtered off and washed with ether. 7.3 g (82%) of *p*-toluenesulphinic acid sodium salt were obtained. The ether was distilled off, the residue was vacuum-distilled. 1.5 g (43%) of **10** with b.p. 70-72° were obtained. Its physical characteristics coincide with those of an authentic sample.[24]

(2) 13.0 g (0.05 mole) of **1c** were boiled in 25 ml of triethylamine for 12 days. The mixture was diluted with ether, and then diluted with HCl (1:1) at 0°. The etheral layer was separated, the aqueous layer was extracted with ether, and the combined etheral soln was washed with a soln of K_2CO_3. The ether was evaporated, the residue was distilled to give 0.8 g (22.6%) of **10**.

Isobutyliden - N,N - dimethylhydrazone **12**. 12.0 g (0.2 mole) of N,N-dimethylhydrazine were added to 25.4 g (0.1 mole) of **1c** in 75 ml ether and left to stand for 12 days at 20°. The mixture was washed with water, the etheral layer was dried with Na_2SO_4, the ether was evaporated, the residue was distilled in vacuum to give 8.0 g (70.2%) of **12**. Its physical characteristics agree with those of a sample obtained according to ref. 25.

Isobutylidene - N - methylhydrazone **13**. (1) 11.0 g (0.25 mole) of monomethylhydrazine was added to a soln of 25.4 g (0.1 mole) of **1c** in 75 ml of ether and left to stand for 2 days at 20°. The mixture was treated with water, the etheral layer was separated and dried with Na_2SO_4. The ether was evaporated under atmospheric pressure, the residue was vacuum-distilled to give 4.2 g (42%) of **13**. Its physical properties agree with those of an authentic sample.[26]

(2) Similarly, 25.4 g (0.1 mole) of **1c** and 12.0 g (0.2 mole) of N,N'-dimethylhydrazine in 30 ml of ether gave 4.3 g (43%) of **13**.

N-*Benzylidenepropylamine*. A mixture of 39.0 g (0.135 mole) of **1d** and 17.7 g (0.3 mole) of *n*-propylamine in THF was stirred for 65 hr at 60°. The mixture was evaporated under vacuum, treated with 150 ml ether, filtered from the ppt salt and evaporated in a rotary vacuum evaporator. The residue was vacuum-distilled to give 13.4 g (68%) of N-benzylidenepropylamine. Its physical characteristics coincide with those of a sample obtained according to ref. 27.

N - *Butylacetamide* - N' - *phenylhydrazone* **16**. A mixture of 21.2 g (0.078 mole) of **1f** and 11.4 g (0.156 mole) of *n*-butylamine in 50 ml CH_2Cl_2 was kept for 6 days at 20°. The mixture was treated with water, the organic layer was dried with $MgSO_4$, the solvent was evaporated, the residue was vacuum-distilled to give 6.5 g (31.5%) of 16, b.p. 128–130°/1 mm; n_D^{20} 1.5818. IR spectrum: 1640 (C=N); 3290, 3350 (NH); 1610 (Ph). ^{1}H NMR: 0.82 (3H, t); 1.4 (4H, m); 1.85 (3H, s, CH_3–C=); 2.95 (2H, t); 6.9 (7H, m).

A *p*-methoxyphenylisocyanate derivative of N - butylacetamide - N' - phenylhydrazone, had m.p. 105–107° from methylene chloride-ether mixture. (Calc: C, 67.76; H, 7.39; N, 15.81. $C_{20}H_{26}N_4O_2$: Found: C, 67.82; H, 7.28; N, 16.23%).

N - n - *butylbenzamide.* 5.4 g (0.074 mole) of *n*-butylamine were added to a soln of 9.0 g (0.038 mole) of N - benzoyl - N - phenylhydrazone of acetaldehyde[20] in 25 ml CH_2Cl_2. The mixture was kept for 30 days at 20°. The solvent was evaporated, the residue was vacuum-distilled, a fraction with b.p. 135–140°/2 mm was collected from which N - *n* - butylbenzamide was isolated by means of a preparative tlc (alumina of II activity grade, ether, R_f 0.645). Its physical characteristics agree with those of a sample prepared according to ref. 29.

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