Tetrahedron Vol. 41, No. 3, pp. 575 to 584, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00

ASYMMETRICAL NITROGEN—40;† GEMINAL SYSTEMS—26.‡ N-CHLOROHYDRAZINES§

G. V. SHUSTOV,* N. B. TAVAKALYAN and R. G. KOSTYANOVSKY
Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

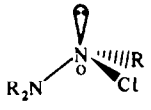
(*Received in UK* 12 *April* 1984)

Abstract—The factors determining the kinetic and thermodynamic stabilities of N-chlorohydrazines are discussed. Acyclic N-chlorohydrazines exist only as trialkyldiazenium chlorides **3a,b**. Chlorination of 2-acyl-1,1-dimethylhydrazines **6a,b** gave 1,4-diacyl-2,3-dimethylhexahydro-1,2,4,5-tetrazines **7a,b** via hydrazyl radical intermediates, and chlorination of a 1-phenylpyrazolidin-5-one **8** gave phenylazoisovaleric esters **9a,b**. Stable N-chlorohydrazines were obtained from bicyclic hydrazines; viz. the 2-chloro-1,2-diazabicyclo [2.2.2]octan-3-one **12** and 7-chloro-1,7-diazabicyclo[2.2.1]heptane **16**. The restricted inversion of N(7) in **16** and its 1-methyl quaternary salt **21** were observed in the ^{13}C-NMR spectra. The acyclic N-chlorohydrazinium salt **25** was isolated.

The inversion barrier of a tricoordinated N atom is considerably increased by the introduction of R_2N—, RO— or halogen substituents.[4] This phenomenon is accounted for by an increase in the nitrogen lone pair s-character in accordance with the Bent–Walsh rule[4–6] or by a stronger geminal n–σ^* interaction[6] from the standpoint of PMO theory. A destabilizing four-electron interaction between a lone pair on a heteroatomic ligand and the inverting N atom is of great importance too.[7]

It is natural to suppose, from the established configurational stability of N-methoxyisoxazolidines,[8a,b] N,N-dialkoxyamines and N-alkoxy-N-chloroamines,[8b,c] that two heteroatomic ligands would stabilize the nitrogen pyramid to a great extent.

In the present work we studied the possibility of obtaining N-chlorohydrazines, a new geminal system with a stable chiral nitrogen pyramid.[3]



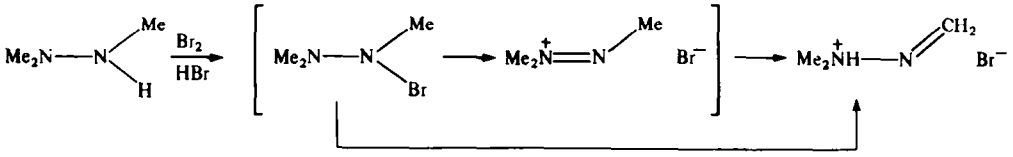
The chlorination of trialkylhydrazines is the simplest approach to such substances. Previously, halogenation has been studied mainly for 1,1-dialkylhydrazines, forming 1,1-dialkyldiazenium salts stable only in acid medium.[9] Bromination of trimethylhydrazine leads to formaldehyde dimethylhydrazone either by dehydrobromination[9d] or through trimethyldiazenium bromide (Scheme 1).

We have synthesized the 2-t-alkyl-1,1-dimethylhydrazines **1a,b**, having no α-proton on the N(2) substituent (Scheme 2).

Chlorination of **1a,b** in CF_3CO_2H affords the diazenium salts **3a,b** (Scheme 3),[3a,b] as shown by the strong deshielding of the N—Me groups in the ^{1}H-NMR spectrum and their nonequivalence due to N=N double bond formation (Table 1).

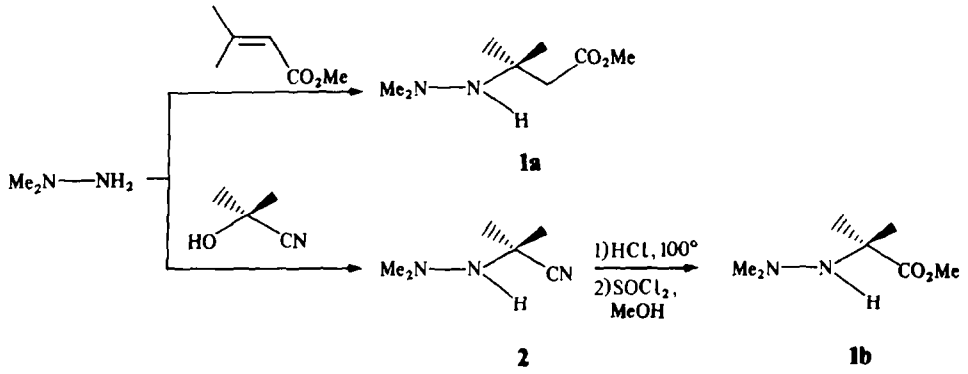
In the case of the trialkyldiazenium chloride **3a** this nonequivalence of N—Me groups ($\Delta\nu = 4.5$ Hz) persists on heating up to 80° (complete sample destruction), whereas for 1,1-dialkyldiazenium bromides $R_2\overset{+}{N}{=}NH\ \bar{B}r$ (R = Me, Et, i-Pr) the coalescence temperature of the R substituent signals lies between 0° and −40° ($\Delta\nu_c$ = 4–14 Hz),[9e] which seems to imply here fast NH exchange at N(2). Heating to 70° does not affect the ^{1}H-NMR spectrum of the diazenium chloride **3b** either. It should be noted that the thermal stability of trialkyldiazenium cations falls with increase in N(2) α-substituent electronegativity. So, the time for complete decomposition of the isobutyric ester derivative **3b** is shorter than for the isovaleric ester **3a** at the same temperature. Chlorination of the α-hydrazoisobutyronitrile **2** under the same conditions as for the esters **1a,b** leads to decomposition products of the corresponding diazenium salt, according to the ^{1}H-NMR spectra.

Thus, acyclic N-chlorotrialkylhydrazines exist only in ion paired forms as trialkyldiazenium chlorides. The reason of this seems to lie in the easy N—Cl bond dissociation and the higher thermodynamic stability of the diazenium cation in solution. As we showed earlier,[8b] the chemical and stereochemical properties of nitrogen geminal systems X—N—Y are defined to a considerable degree by the vicinal n–σ^* interaction (Fig. 1). This interaction is commonly a thermodynamically stabilizing factor because of its effect in lowering

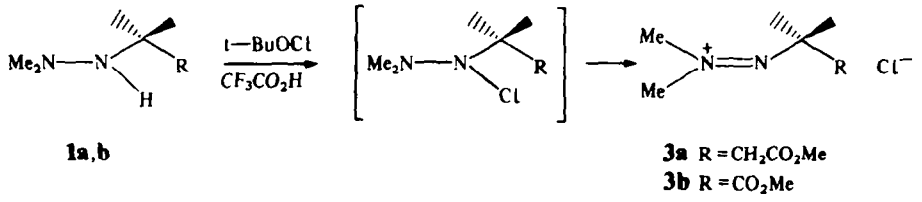


Scheme 1.

† Communication 39, see ref. 1.
‡ Communication 25, see ref. 2.
§ Preliminary communication, see ref. 3.



Scheme 2.



Scheme 3.

the nonbonding orbital energy of a donor group (X) and so reducing the total molecular energy.[8b,10] However, the n–σ^* interaction increases the σ-antibonding orbital population of the N—Y bond (acceptor), weakens this bond, and consequently decreases the kinetic stability of X—N—Y systems.

The combination of a powerful n-donor such as an amino group, with a Cl atom, a strong σ-acceptor (leaving group), leads to the most significant kinetic destabilization.[8b] In addition, an orbital destabilizing interaction between lone pairs of three bonded heteroatoms (Fig. 2), described earlier in detail for the O—N—O system,[7a] seems to decrease N-chlorohydrazine stability.

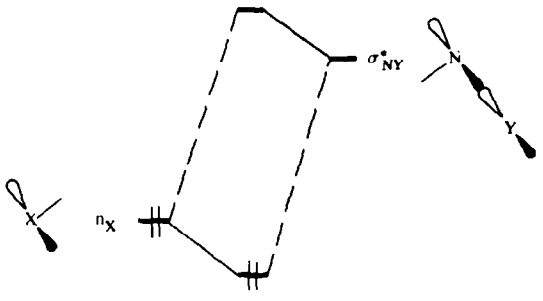


Fig. 1.

Table 1. ^{1}H-NMR spectra (80 MHz) of the trialkylhydrazines **1a,b**, **2**, the acylhydrazines **6a,b** and the chlorination products of these compounds—the diazenium chlorides **3a,b** and hexahydrotetrazines **7a,b**

	Compound R	δ MeN	δ CMe_2	δ R	δ Other	Solvent
1a	CH_2CO_2Me	3.13	1.42	2.88 (CH_2), 3.85 (MeO)	—	CF_3CO_2H
1b	CO_2Me	2.86	1.12	3.46	—	CF_3CO_2H
2	CN	3.28	1.61	—	—	CF_3CO_2H
3a	CH_2CO_2Me	4.46 and 4.52	1.73	3.26 (CH_2), 3.82 (MeO)	—	CF_3CO_2H
3b	CO_2Me	3.88 and 4.30	1.54	3.51	—	CF_3CO_2H
6a	Me *Z* (42%)	2.54	—	1.77	9.00 (NH)	CCl_4
	E (58%)	2.50	—	1.95	8.60 (NH)	
6b	CH_2Ph *Z* (45%)	2.48	—	3.48 (CH_2), 7.27 (Ph)	6.45 (NH)	$CDCl_3$
	E (55%)	2.40	—	3.76 (CH_2), 7.27 (Ph)	6.45 (NH)	
7a	Me	2.60	—	2.14	4.33 (H_A), 4.90 (H_B) J_{AB} = 13 Hz	$CDCl_3$
7b	CH_2Ph	2.38	—	3.78 (CH_2), 7.27 (Ph)	4.06 (H_A), 5.10 (H_B) J_{AB} = 13.5 Hz	$CDCl_3$

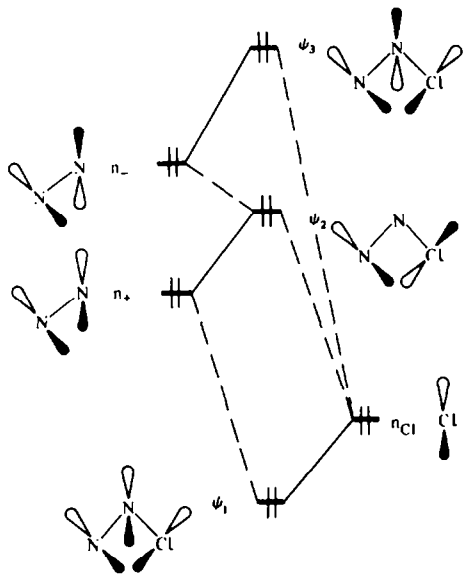
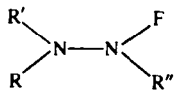


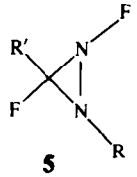
Fig. 2.

Consequently, the minimization of the six-electron interaction, and in particular the vicinal n–σ^* interaction, is the main precondition for the existence of N-chlorohydrazines and in general of hydrazines with σ-acceptor substituents. This minimization can be effected in one of the following ways: (a) introduction of an electron-withdrawing substituent on the N(2) atom (bonded to the Cl), thus lowering the n-orbital level of this atom and decreasing the N—Cl bond acceptor capacity by reducing its polarization; (b) lowering of the amino-group donor capacity, either by involving the N(1) lone pair in competitive n–π^* conjugation or by lone pair blocking by quaternization; (c) decreasing the overlap of the N(1) n-orbital with the σ-antibonding orbital of the N(2)—Cl bond and the N(2) n-orbital by steric constraints. One can explain the existence of the N-fluorohydrazines **4**[11] and N-fluorodiaziridines **5**[12] on the above considerations.



4

R = R′ = R″ = F [11a,b]
R = R′ = R″ = CF_3 [11c]
R = F, R′ = R″ = CF_3 [11c]
R + R″ = $(CF_2)_3$, R′ = F [11d]
R = F, R′ = CHF_2, R″ = CF_3 [11d]
R = F, R′ = R″ = Me [11e]
R = F, R′ = R″ = t—Bu [11f]



5

R = CF_3, R′ = NF_2 [12a]
R = F, R′ = NF_2 [12b]
R = R′ = F [12b]
R = CF_2NF_2, R′ = NF_2 [12b]

In all these substances (**4**, **5**) the electron-donor capacity of all the nitrogen lone pairs is reduced either by competitive hyperconjugation with a perfluoroalkyl group, or by raising the nitrogen lone pair s-character, in the case of the N-fluorine substituent, and also by inclusion of the nitrogen in a 3-membered ring. In tetrafluorohydrazine, the electron-donating capacity of the NF_2 group is lowered to such an extent that N—F bond ionization, yielding the trifluorodiazenium cation, takes place only by the action of Lewis acids.[13] In the present work we report on our attempts to obtain stable N-chlorohydrazines, based on the considerations outlined above.

2-Acyl-2-chloro-1,1-dimethylhydrazines conform to the first condition (a). However, chlorination of the acylhydrazines **6a,b** affords the hexahydrotetrazines **7a,b**, rather than the N-chloro-derivatives.

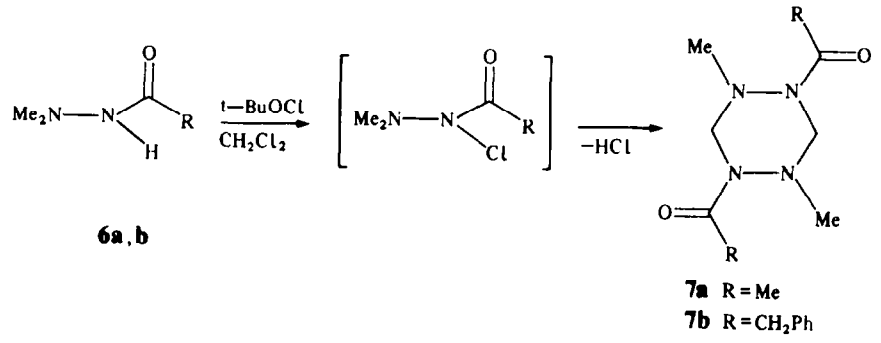
In contrast to the N-acylhydrazines (**6a,b**), *Z,E*-isomers of the 1,4-diacylhexahydrotetrazines (**7a,b**), due to hindered rotation about the N—CO bond, are not observed in the ^{1}H-NMR spectra (Table 1). The *E*-isomer of a 2-acyl-1,1-dialkylhydrazine is usually thermodynamically more stable,[24] therefore we assume the 1,4-diacylhexahydrotetrazines **7a,b** to be *E,E*-isomers. The ring proton geminal nonequivalence seems to arise from restricted ring conversion, which is equivalent to restricted N—N bond rotation, because the observed $\Delta G^{\ddagger}$ values [18.0 kcal/mol, $\Delta\nu_c$ = 17.5 Hz, T_c = 84° in $(CD_3)_2SO$ for **7a** and 19.0 kcal/mol, 84 Hz, 115° in Ph_2O for **7b**] are similar to the N—N bond rotation barriers of 2-acyl-1,1-dialkylhydrazines (17 kcal/mol).[14a]

It is known that 1,4-diacyl-2,5-dimethylhexahydro-1,2,4,5-tetrazines are obtained on oxidation of 2-acyl-1,1-dimethylhydrazines by HgO, $Pb(OAc)_4$ or S_2Cl_2,[15a] or by condensation of 2-acyl-1-methylhydrazines with formaldehyde.[15b,c] Therefore, one may suppose a common scheme for hexahydrotetrazine formation by dimerization of the dipole A, formed from the hydrazyl radical, or by hydroxymethylhydrazine dehydration (Scheme 5).

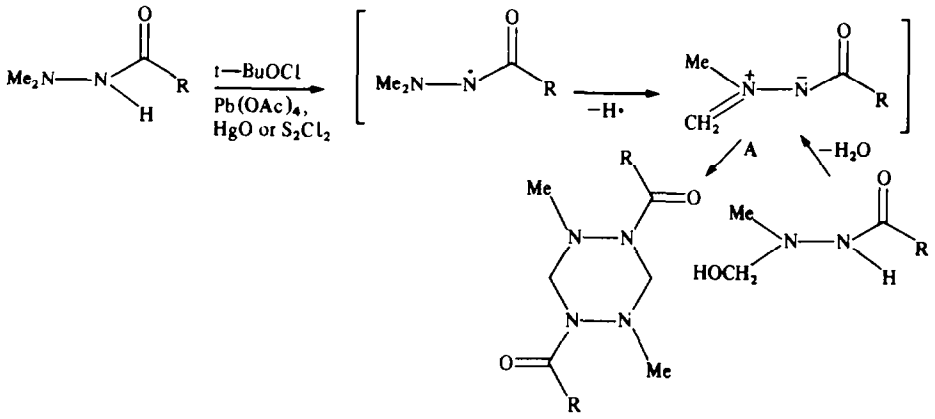
The hydrazyl radical can be observed by ESR on reaction of t-BuOCl with 1,1-diphenyl-2-picrylhydrazine (Scheme 6).

Thus, the N—Cl bond depolarization of the π-acceptor ligand at N(2) facilitates the homolysis of this bond. The thermodynamic preference for this route to N-chlorohydrazide decomposition is due to captodative stabilization[16] of acylhydrazyl radicals.

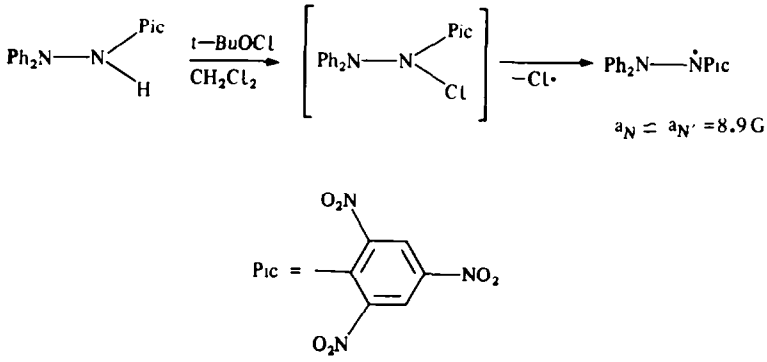
The first condition (a) is consequently insufficient to provide a stable N-chlorohydrazine. We therefore studied the chlorination of the pyrazolidinone **8**, a cyclic hydrazine with π-acceptor substitution at the donor N atom, to investigate the effectiveness for stabilization of condition (b).



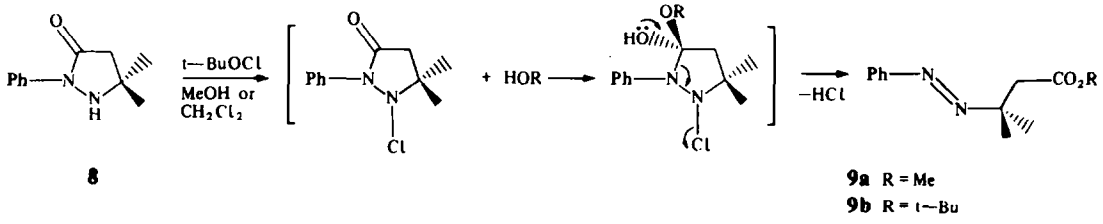
Scheme 4.



Scheme 5.



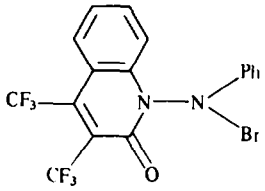
Scheme 6.



Scheme 7.

We find that the reaction of **8** with t-BuOCl in MeOH yields only the azo-compound **9a**, the product of methanolysis of the N-chloro-derivative (Scheme 7). Such a transformation was earlier observed during chlorination of O-benzoyl-N-tert-butylhydroxylamine in MeOH. Nevertheless, O-benzoyl-N-tert-butyl-N-chloro-hydroxylamine was obtained in such inert solvents as CH_2Cl_2 and Et_2O.[17] We were, however, unsuccessful in obtaining the N-chloropyrazolidinone under these conditions; this compound evidently reacts even with the sterically hindered t-BuOH (Scheme 7). This may be explained by the strong activation of the carbonyl group on introduction of the Cl atom, as a result of a partial positive charge on the neighbouring N atom due to n–σ^* hyperconjugation.

In view of this finding, the observation[18] that the N-bromohydrazide **10** is stable towards MeOH is surprising.



10

The third condition (c) is fulfilled in the case of bicyclic hydrazines with bridgehead donor nitrogen because their conformation, unsuitable for overlap of the n-orbital with the vicinal σ^*_{NCl} orbital, is rigid. Such an n_N–σ^*_{NCl} interaction is possible in the planar transition state of the N—Cl fragment inversion (Scheme 8). However, it does not lead to considerable overlap gain, firstly, because of the smaller absolute value of a *cis* overlap integral in comparison to a *trans*,[6b] and secondly, the σ-bond acceptor capacity decreases considerably as the nitrogen becomes planar.[8b]

Actually, chlorination of 2-azaquinuclidone **11** affords the stable N-chloro-derivative **12** (Scheme 9) with planar N(2) configuration according to the C(5)/C(8) and C(6)/C(7) signal coincidences in the ^{13}C-NMR spectrum (Table 2).

The similarity of $\nu_{C=O}$ frequencies in the IR spectra of the N-chlorohydrazide **12** (1690 cm^{-1}) and its precursor **11** (1685 cm^{-1}) indicates the presence of the amide n–π^*_{CO} conjugation, stabilizing the planar state (Scheme 9).

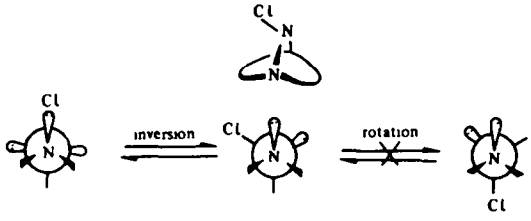
The N-chlorohydrazide **12** is dechlorinated by excess of Me_2NH under mild conditions (0 to −5°); in the absence of n–π^*_{CO} conjugation N—CO bond rupture by nucleophilic attack at the activated CO group would be expected (Scheme 10).

The electronegativities of N and Cl atoms are similar[19]—4.49 and 4.93; N—Cl σ-bond polarization and therefore N-chloroamine reactivity is affected by the other N-substituents. In chloramine (NH_2Cl) and its alkyl derivatives the N—Cl bond is normally polarized towards the more electronegative Cl atom[19b,c] and nucleophilic attack takes place at the N atom, with the higher AO contribution into the antibonding σ^*_{NCl} orbital (Scheme 11a). Thus, these compounds act as aminating reagents.[20a,b] The chlorinating action of N-chloroamides (e.g. N-chlorosuccinimide[20c]) and the N-chlorohydrazide **12** one can explain in terms of N—Cl bond polarization towards the positive N atom[19c] with its lone pair included in the amide conjugation. Therefore, the Cl atom, the larger coefficient of the antibonding σ^*_{NCl} orbital, experiences preferential nucleophilic attack (Scheme 11b).

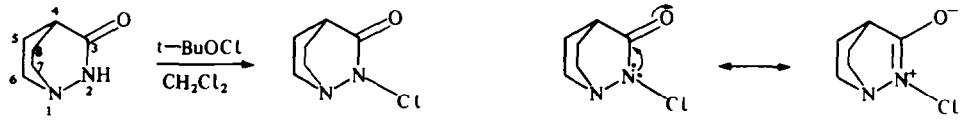
The stable N-chlorohydrazine **16** with a pyramidal N atom was obtained by the action of t-BuOCl upon 1,7-diazabicyclo[2.2.1]heptane **15** (Scheme 13), itself obtained by an intramolecular cycloaddition route (Scheme 12).

Compound **16** was also obtained by chlorinolysis of the methylenebishydrazine **18**, the product of disproportionation of the hydroxymethyl derivative **17** (Scheme 13).

The restricted inversion of the N(7) atom in the N-chlorohydrazine **16** follows from the C(2)/C(6) and C(3)/C(5) nuclear nonequivalence in the ^{13}C-NMR spectrum (Table 2). The above signals do not coalescence up to 120° in $PhNO_2$ (when the sample is completely decomposed). The inversion barrier is estimated from $\Delta\nu = 9.3$ Hz at 120° to be not lower than 22.8 kcal/mole. This value is reasonable, when compared with the $\Delta G^{\ddagger}_{inv}$ values for the bicyclic N-



Scheme 8.



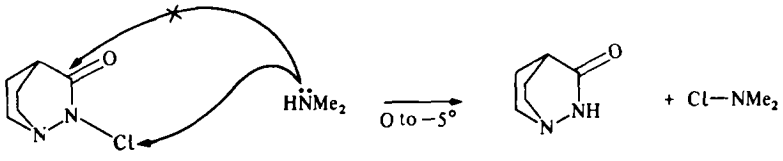
11 **12**

Scheme 9.

Table 2. ^{13}C-NMR spectra* of the bicyclic hydrazines **11**, **12**, **15**, **16** and **21**, **22** in $CDCl_3$

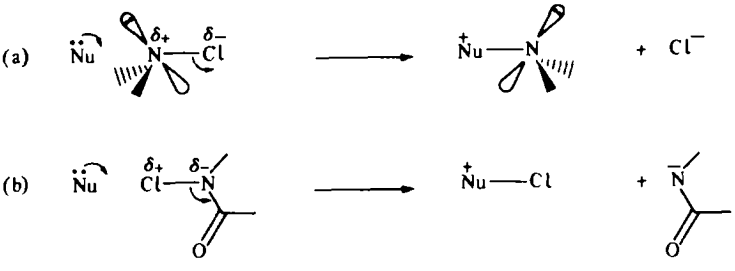
Compound	R	δ						
		C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
11	H	—	s 179.81	d 34.65	t 26.23	t 51.34	t 51.34	t 26.23
12	Cl	—	s 176.22	d 38.21	t 26.62	t 51.18	t 51.18	t 26.62
15	H	t 55.27	t 31.83	d 56.69	t 31.83	t 55.27	—	—
16	Cl	t 52.12	t 28.71	d 68.86	t 29.42	t 52.59	—	—
21†	Cl	t 61.40	r 23.46	d 59.00	t 28.30	t 70.40	—	q 42.60
22†	H	t 63.00	t 28.83	d 56.20	t 28.83	t 63.00	—	q 43.76

* Incomplete H-decoupling (off resonance).
† δ_{TsO^-} : 18.5 (q, Me), 127.2 (d, C-3, 5), 130.4 (d, C-2, 6), 141.4 (s, C-4), 146.3 (s, C-1).

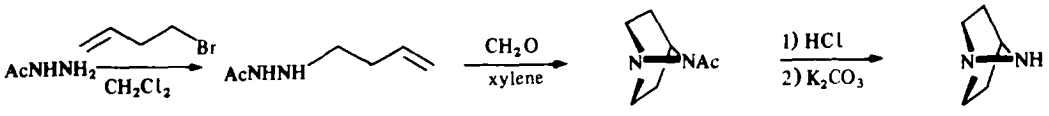


12 **11**

Scheme 10.

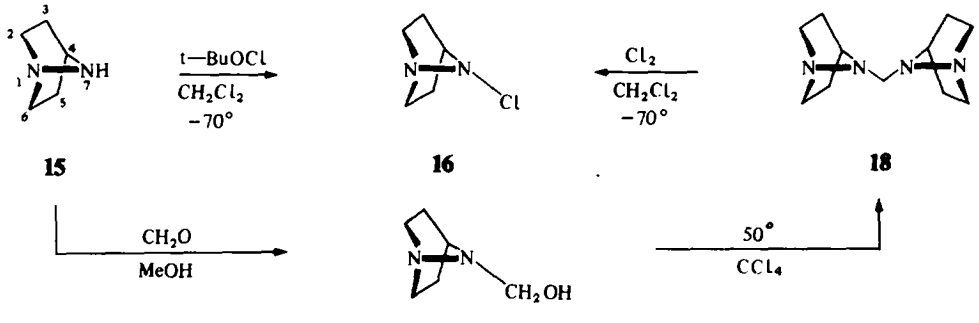


Scheme 11.



13 **14** **15**

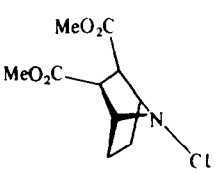
Scheme 12.



15 **16** **18** **17**

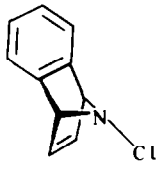
Scheme 13.

chloroamines **19**, **20**, close analogues of the chlorohydrazine **16**.



19

$\Delta G^{\ddagger}_{140°} = 21$ kcal/mole[4]



20

$\Delta G^{\ddagger}_{230} = 23.5$ kcal / mole[22]

The increase in configurational stability of N(7) in **16** is caused mainly by two factors: the inclusion of this atom in the strained bridge, and the presence of Cl and N(1) electronegative ligands. The lone-pair destabilizing interaction can be achieved only along the N—Cl bond because of the orthogonality of the N(1) and N(7) nonbonding orbitals in the transition state of the inversion (Scheme 8).

The N-chlorohydrazine **16** on treatment with methyl tosylate affords the crystalline salt **21** which is easily dechlorinated by brief reflux in MeCOEt or by standing in $CHCl_3$ for 30 days at 20°. The dechlorination both of **21** and of the N-chlorohydrazide **12** (Scheme 10) is determined by N—Cl bond depolarization due to the positive charge at the neighbouring N(1) atom. The reverse transformation, of **22** into the N-chloroderivative **21**, occurs by the action of t-BuOCl (Scheme 14).

The C(2)/C(6) and C(3)/C(5) nonequivalence due to the restricted inversion of N(7) is also observed in the ^{13}C-NMR spectrum of the N-chlorohydrazinium salt **21** (Table 2). Thus, on the evidence from the bicyclic hydrazines **16** and **21**, it should be possible to construct the chiral systems R_2N—N(R)Cl and $R_3\overset{+}{N}$—N(R)Cl.

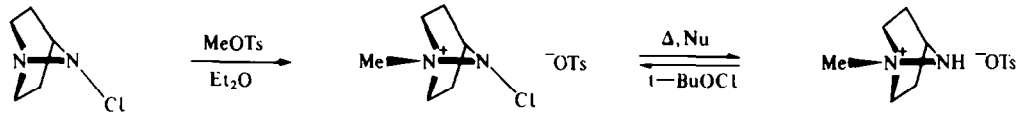
Accordingly, the hydrazinium chloride **23b** was prepared (Scheme 15). However, in contrast to **22**, compound **23b** was unchanged by t-BuOCl in MeOH at 20°. This is probably because of steric screening of the NH group by the bulky $Me_3\overset{+}{N}$— and MeO_2CCMe_2— substituents. In fact, the sterically less hindered 1,1,1-trimethylhydrazinium tosylate **24** easily forms the N-chlorohydrazinium salt **25**.

Consequently, it is possible to realize the second principle (b—*vide supra*) too—to construct a hydrazine with an N—Cl covalent bond by the blocking of the lone pair of the donor nitrogen by quaternization.

UV-absorption is an important characteristic of N-chlorohydrazines (Table 3). The band in the range 240–250 nm in the UV spectra of the N-chlorohydrazines **12** and **16** undergoes a blue shift on change of solvent from heptane to MeOH. This allows attribution of this band to an n–σ^* transition, as in the case of N-chloroamines.[23]

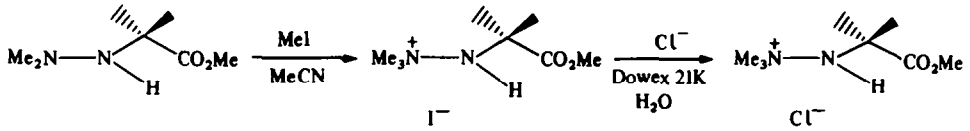
Electrons of the doubly-degenerate nonbonding level of the Cl atom were suggested[24] to take part in the n–σ^* transition of the chloroamine chromophore. However, from the PE spectral data of MeNHCl and Me_2NCl, and from *ab initio* and SPINDO calculations,[25] it follows that four-electron interaction with the nitrogen lone pair removes the degeneracy of the Cl n-orbitals. In this case the antisymmetric combination (n_N–n_{Cl}) with higher n_N contribution is HOMO.[25b] Therefore, the absorption of the N-chloroamine chromophore is caused by the electron transition from the n_N–n_{Cl} HOMO into the σ^*_{NCl} LUMO.

A similar transition can be expected for the N-chlorohydrazines **12** and **16**, neglecting the N(1) n-orbital interaction with the N—Cl fragment. A blue shift of the n–σ^* band for the hydrazine **16** (λ_{max} 253 nm) and a larger blue shift for the hydrazinium salt **21** (λ_{max} 237 nm) in comparison with dialkyl-N-chloroamines (λ_{max} 260–270 nm)[23] reflects the inductive effect of the



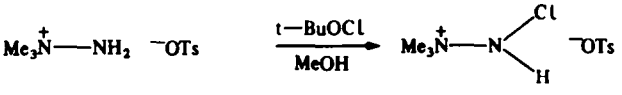
16 **21** **22**

Scheme 14.



1b **23a** **23b**

Scheme 15.



24 **25**

Scheme 16.

Table 3. UV spectra of N-chlorohydrazines

Compound	Solvent	λ, nm	log ε
12	Heptane	246	3.05
	MeOH	243	2.93
16	Heptane	253	2.70
	MeOH	250	2.70
21*	H_2O	237†	2.67
23*	H_2O	241†	3.40

* $\lambda_{max}^{TsO^-}$ = 223 nm (log ε ~ 4.1).
† Absorption of the N—Cl chromophore was measured by substruction of UV spectrum of the corresponding NH-compound **22** or **24**.

N(1) atom and the increase in s-character of the N(7) n-orbital as a result of the inclusion of this atom into the strained bridge. The latter explains the shorter-wave absorption of the N—Cl chromophore of the bicyclic salt **21** in comparison to the acyclic **25** (Table 3). The n–π^*_{CO} interaction in **12** lowers the n-orbital level so that the n–σ^* band for **12** to shorter-wavelength as of that of the N-chlorohydrazine **16**.

EXPERIMENTAL

The NMR spectra were obtained on BS-487C (^{1}H, 80 MHz), JNM-C-60HL (^{1}H, 60 MHz, int. standard HMDSO) and XL-100 (^{13}C, 25.2 MHz, int. standard TMS) spectrometers; IR and UV spectra—on UR-20 (in thin films for liquid samples and in KBr pellets for solids) and Specord UV VIS spectrophotometers, respectively, and mass-spectra on a MH-1303 spectrometer (30 eV).

Methyl β-(N,N-dimethylhydrazino)isovalerate (**1a**). A mixture of methyl β,β-dimethylacrylate (10.3 g, 0.09 mol) and 1,1-dimethylhydrazine (DMH) (13.2 g, 0.22 mol) was heated in a sealed ampoule for 96 hr at 100°, yielding, after distillation, the initial dimethylacrylate (6.81 g, 0.06 mol), b.p. 60°/50 mm, and **1a** (3.9 g, 75%), b.p. 66–68°/18 mm, n_D^{20} 1.4342. (Found: C, 55.15; H, 10.2; N, 16.1. $C_8H_{18}N_2O_2$ requires C, 55.15; H, 10.4; N, 16.1%.) IR: ν 1720 (CO), 3440 cm^{-1} (NH).

N,N-Dimethylhydrazinoisobutyronitrile (**2**). 2-Cyano-2-propanol (8.5 g, 0.1 mol) and DMH (7.5 g, 0.125 mol) were mixed and left to stand 48 hr at 20°. The organic layer was separated, dried over $MgSO_4$ and distilled *in vacuo*, providing **2** (10.4 g, 82%), b.p. 70–71°/30 mm, n_D^{20} 1.4255. (Found: C, 56.45; H, 10.2; N, 33.1. $C_6H_{13}N_3$ requires: C, 56.7; H, 10.3; N, 33.0%.) IR: ν 3450 cm^{-1} (NH).

Methyl N,N-dimethylhydrazinoisobutyrate (**1b**). The nitrile **2** (10.4 g, 0.082 mol) in conc. HCl (50 ml) was kept 24 hr at 20° and 1.5 hr at 100°. After removal of HCl excess the solid was dissolved in MeOH (100 ml). To this $SOCl_2$ (19.0 g, 0.16 mol) was added dropwise with cooling (10–15°) and stirring. After reflux 1.5 hr the solvent was removed *in vacuo* and the residue was treated with satd K_2CO_3 aq. The product was extracted into Et_2O and dried ($MgSO_4$). After removal of solvent the residue was distilled *in vacuo*, providing ester **1b** (8.1 g, 62%), b.p. 77–80°/30 mm. (Found: C, 52.7; H, 10.1; N, 17.5. $C_7H_{16}N_2O_2$ requires: C, 52.5; H, 10.1; N, 17.5%.) IR: ν 1715 (CO), 3440 cm^{-1} (NH).

Chlorination of the N'-t-alkyl-N,N-dimethylhydrazines (**1a,b**, **2**). To a soln of the hydrazine (0.1–0.2 mmol) in CF_3CO_2H (0.3–0.5 ml) in a 5 mm ampoule was added t-BuOCl (0.2–0.4 mmol), with cooling (0 to −5°); the ^{1}H-NMR spectrum (Table 1) was recorded at 30°.

Chlorination of 2-acetyl-1,1-dimethylhydrazine (**6a**). A soln of t-BuOCl (1.09 g, 0.01 mol) in CH_2Cl_2 (3 ml) was added dropwise to a cooled (−15°) stirred suspension of K_2CO_3 (1.38 g, 0.01 mol) in CH_2Cl_2 (15 ml) containing **6a**[26] (1.02 g, 0.01 mol). After the stirring 1.5 hr at 20° the mixture was washed with water and dried ($MgSO_4$). After solvent removal the residue was crystallized from MeOH. Compound **7a** (0.12 g, 55%), m.p. 160–161° (lit.[15c] m.p. 160°) was obtained. IR: ν 1647 cm^{-1} (CO). The starting hydrazine **6a** (0.8 g) was obtained from the mother liquor.

Chlorination of 2-phenylacetyl-1,1-dimethylhydrazine (**6b**) was carried out as above. Compound **7b** (0.2 g), m.p. 202–203° (from EtOAc) (lit.[15b] m.p. 203–204°) was obtained from **6b**[27] (1.78 g, 0.01 mol). IR: ν 1658 cm^{-1} (CO).

Chlorination of 1,1-diphenyl-2-picrylhydrazine (DPPH). t-BuOCl (0.2 g, 1.9 mmol) was added to a cooled (−60 to −70°) and stirred suspension of K_2CO_3 (0.25 g, 1.8 mmol) in CH_2Cl_2 (20 ml) containing DPPH (0.59 g, 1.5 mmol) and Et_3N (0.18 g, 1.8 mmol). After 0.5 hr at 0° the mixture was washed with water and dried (K_2CO_3). After solvent removal the residue (dark-violet crystals) was dissolved in benzene and the ESR spectrum was recorded.

3,3-Dimethyl-1-phenylpyrazolidin-5-one (**8**). A mixture of phenylhydrazine (6.8 g, 0.063 mol) and methyl β,β-dimethylacrylate (7.2 g, 0.063 mol) was kept under N_2 for 95 hr at 140°. The product was extracted with Et_2O and after solvent removal was recrystallized from Et_2O–hexane. Pyrazolidinone **8** (1.52 g, 13%), m.p. 71–72.5°, was obtained. (Found: C, 69.15; H, 7.4; N, 14.9. $C_{11}H_{14}N_2O$ requires: C, 69.35; H, 7.4; N, 14.7%.) IR: ν 1685 (CO), 3196 cm^{-1} (NH). UV $\lambda_{max}^{heptane}$ nm (log ε): 205 (3.22), 260 (3.06). ^{1}H-NMR (CCl_4): δ 1.16 (Me_2C), 2.17 (CH_2), 4.30 (NH), 7.00 and 8.07 (m, Ph).

Chlorination of the pyrazolidinone (**8**)

(a) *In* MeOH. t-BuOCl (0.3 g, 2.8 mmol) was added with cooling (−60 to −70°) to **8** (0.38 g, 2 mmol) in abs. MeOH (10 ml). After 0.5 hr at −70° the MeOH was evaporated *in vacuo* and the residue was chromatographed on silica ($CHCl_3$). Compound **9a** (0.33 g, 75%) was isolated. (Found: C, 65.4; H, 7.5; N, 12.5. $C_{12}H_{16}N_2O_2$ requires: C, 65.4; H, 7.3; N, 12.7%.) IR: ν 1730 cm^{-1} (CO). UV $\lambda_{max}^{heptane}$ nm (log ε): 213 (3.05), 262 (2.92), 411 (1.04, n–π^*_{NN}). ^{1}H-NMR (CCl_4): δ 1.34 (Me_2C), 2.55 (CH_2), 3.48 (MeO), 7.30 (m, Ph).

(b) *In* CH_2Cl_2. Compound **9b** (0.94 g, 72%) was obtained from **8** (0.95 g, 5 mmol) and t-BuOCl (0.6 g, 5.5 mmol) in CH_2Cl_2 (10 ml) as described above. (Found: C, 68.5; H, 8.5; N, 10.6. $C_{15}H_{22}N_2O_2$ requires: C, 68.6; H, 8.5; N, 10.7%.) IR: ν 1710 cm^{-1} (CO). UV $\lambda_{max}^{heptane}$ nm (log ε): 213 (3.09), 262 (2.95), 411 (1.06, n–π^*_{NN}). ^{1}H-NMR (CCl_4): δ 1.30 (Me_3C), 1.32 (Me_2C), 2.47 (CH_2), 7.35 (m, Ph).

2-Chloro-1,2-diazabicyclo[2.2.2]octan-3-one (**12**). t-BuOCl (0.76 g, 7 mmol) in CH_2Cl_2 (2 ml) was added dropwise with cooling (−60 to −70°) and stirring to **11**[28] in CH_2Cl_2 (15 ml). After 0.5 hr at 20° the solvent was evaporated *in vacuo* and the residue sublimed at 80°/1 mm, giving **12** (0.75 g, 94%), m.p. 118–119°. (Found: C, 44.7; H, 5.55; N, 17.3. $C_6H_9ClN_2O$ requires: C, 44.9; H, 5.65; N, 17.4%.) ^{1}H-NMR ($CDCl_3$): δ 1.93 (m, CH_2C), 3.13 (m, CH_2N, CH). MS *m/z* (rel. int., %): 162, 160 (M^+ 5, 13), 134, 132 (7, 23), 125 (13), 117 (3), 106, 104 (6, 13), 97 (65), 83 (33), 69 (77), 55 (100), 41 (83).

Dechlorination of **12** *by dimethylamine.* The chlorohydrazide **12** (0.16 g, 1 mmol) in Me_2NH (0.5 ml) was kept for 0.5 hr at 0 to −5° and Me_2NH was evaporated at 20°. The hydrazide **11** (0.13 g, 100%), m.p. 171–173° (lit.[28] m.p. 171–173°) was obtained.

1-Acetyl-2-(but-3-enyl)hydrazine (**13**). 4-Bromobut-1-ene (13.5 g, 0.1 mol) and acetylhydrazine (22.2 g, 0.3 mol) in DMF (200 ml) was kept for 72 hr at 20° and solvent was evaporated *in vacuo* at 60°/16 mm. After treatment with satd K_2CO_3 aq the product was extracted into $CHCl_3$ and dried ($MgSO_4$). After solvent removal the residue was distilled *in vacuo* giving **13** (8.32 g, 65%), b.p. 108–109°/1 mm. (Found: N, 21.8. $C_6H_{12}N_2O$ requires: N, 21.7%.) ^{1}H-NMR (60 MHz, CCl_4): δ 1.84 (MeCO), 2.17 (broad t, CH_2), 2.75 (t, CH_2N, J = 7 Hz), 4.49 (broad s, NH), 4.96 (m, CH_2=), 9.15 (NHCO).

7-Acetyl-1,7-diazabicyclo[2.2.1]heptane (**14**). A soln of **13**

(12.8 g, 0.1 mol) and paraformaldehyde (6.0 g, 0.2 mol) in *p*-xylene (350 ml) reflux with water-separator for 4 hr. After addition of more paraformaldehyde (1.5 g), reflux was continued for 40 hr. After solvent removal at 60–70°/16 mm the residue was distilled *in vacuo*, providing **14** (6.3 g, 45%), b.p. 65–67°/1 mm. (Found: N, 20.0. $C_7H_{12}N_2O$ requires: N, 20.0%.) IR: ν 1670 cm^{-1} (CO). ^{1}H-NMR (60 MHz, CCl_4): δ 1.54 (m, CH_2C), 1.94 (MeCO), 2.69 (m, CH_2N), 4.63 (t, CH, J = 4.5 Hz).

1,7-*Diazabicyclo*[2.2.1]*heptane* (**15**). The acetyl derivative **14** (2.45 g) was refluxed 3 hr in conc HCl (20 ml). After removal of HCl excess the residue was treated with satd KOH aq and the product was extracted with Et_2O and dried (K_2CO_3). After solvent removal the residue was distilled *in vacuo*, providing **15** (1.27 g, 74%), b.p. 75–77°/30 mm, n_D^{20} 1.4922. (Found: C, 61.2; H, 10.2; N, 28.4. $C_5H_{10}N_2$ requires: C, 61.2; H, 10.3; N, 28.5%.) IR: ν 3370 cm^{-1} (NH). UV $\lambda_{max}^{heptane}$ nm (log ε): 206 (2.83). ^{1}H-NMR (60 MHz, CCl_4): δ 1.38 (m, CH_2C), 2.53 (m, CH_2N), 3.44 (NH), 3.75 (t, CH, J = 4.5 Hz).

The hydrazine **15** on treatment with PhCOCl in Schotten–Baumann conditions affords the N-benzoyl derivative (yield 60%, m.p. 78–80° from Et_2O–hexane). (Found: C, 71.4; H, 7.0; N, 13.8. $C_{12}H_{14}N_2O$ requires: C, 71.3; H, 6.98; N, 13.9%.) IR: ν 1634 cm^{-1} (CO). ^{1}H-NMR (80 MHz, CCl_4): δ 1.31 and 1.88 (m, CH_2C), 2.50 and 2.90 (m, CH_2N), 4.73 (t, CH, J = 4.5 Hz), 7.49 and 7.78 (m, Ph).

7-*Chloro*-1,7-*diazabicyclo*[2.2.1]*heptane* (**16**). t-BuOCl (0.75 g, 6.9 mmol) in CH_2Cl_2 (5 ml) was added dropwise with cooling (−70°) and stirring to **15** (0.6 g, 6.1 mmol) in CH_2Cl_2 (10 ml). After 40 min at −70° the solvent was evaporated *in vacuo* and the residue was distilled, providing **16** (0.5 g, 62%), b.p. 53°/1 mm, n_D^{20} 1.5142. (Found: C, 45.45; H, 6.8; N, 21.2. $C_5H_9N_2Cl$ requires: C, 45.3; H, 6.8; N, 21.1%.) ^{1}H-NMR (60 MHz, CCl_4): 2.25 (m, CH_2CH_2N), 3.80 (t, CH, J = 4.5 Hz). MS *m/z* (rel. int., %): 134, 132 (M^+, 18, 55), 106, 104 (15, 41), 97 (87), 83 (64), 69 (65), 55 (72), 41 (100), 28 (56).

Reaction of **15** *with formaldehyde.* The hydrazine **15** (0.33 g, 3.4 mmol) in abs. MeOH (5 ml) containing CH_2O (0.11 g, 3.7 mmol) was kept for 10 min at 20°; the solvent was then removed and the residue recrystallized from Et_2O at −70°. Compound **17** (0.31 g, 71%), m.p. 42–47°, was obtained. ^{1}H-NMR (80 MHz, CCl_4): δ 1.20 and 1.78 (m, CH_2C), 2.38 and 2.88 (m, CH_2N), 3.73 (t, CH, J = 4.5 Hz), 4.01 (NCH_2O), 5.40 (OH).

After 1 hr at 50° in CCl_4 the hydroxymethyl-derivative **17** formed the methylene-bishydrazine **18**, which was recrystallized from hexane at −70° and sublimed at 70°/2 mm. (Found for the sample **18** with m.p. 95–96°: N, 26.7. $C_{11}H_{20}N_4$ requires: N, 26.9%.) ^{1}H-NMR (80 MHz, CCl_4): δ 1.16 and 1.78 (m, CH_2C), 2.33 and 2.79 (m, CH_2N), 3.03 (NCH_2N), 3.78 (t, CH, J = 4.5 Hz).

Chlorination of the methylene-bishydrazine **18**. Cl_2 (0.14 g, 2 mmol) was passed through a soln of **18** (0.104 g, 0.05 mmol) in CH_2Cl_2 (2 ml) with cooling (−70°). After 0.5 hr at 20° the mixture was washed with water and dried ($MgSO_4$). After solvent removal the residue was distilled *in vacuo* providing **16** (0.05 g, 78%).

7 - *Chloro* - 1 - *methyl* - 1,7 - *diazabicyclo*[2.2.1]*heptane tosylate* (**21**). A soln of **16** (0.21 g, 1.6 mmol) and methyl tosylate (0.3 g, 1.6 mmol) in abs. Et_2O (10 ml) was kept for 48 hr at 20°. The precipitated crystals were filtered off, washed with Et_2O and dried *in vacuo*. The salt **21** (0.27 g, 53%), m.p. 104–105°, was obtained. (Found: C, 49.8; H, 6.2; N, 8.8. $C_{13}H_{19}ClN_2O_3S$ requires: C, 50.0; H, 6.0; N, 8.8%.) ^{1}H-NMR (60 MHz, CD_3OD): δ 2.14 (m, CH_2C), 2.26 (MeAr), 3.79 (m, CH_2N), 3.30 (MeN), 4.37 (t, CH, J = 4.5 Hz), 7.05 and 7.53 (C_6H_4, J_{AB} = 8.3 Hz).

1 - *Methyl* - 1,7 - *diazabicyclo*[2.2.1]*heptane tosylate* (**22**). Compound **22** (0.49 g, 86%), m.p. 134–135° (from acetone–MeCOEt) was obtained from **15** (0.196 g, 2 mmol) and methyl tosylate (0.373 g, 2 mmol) as described above. (Found: C, 54.9; H, 7.0; N, 9.7. $C_{13}H_{20}N_2O_3S$ requires: C, 54.9; H, 7.1; N, 9.85%.) IR: ν 3430 cm^{-1} (NH). UV $\lambda_{max}^{H_2O}$ nm (log ε): 223 (4.08). ^{1}H-NMR (60 MHz, CD_3OD): δ 2.00 (m, CH_2C), 2.26 (MeAr), 3.44 (m, CH_2N), 3.31 (MeN), 4.09 (t, CH, J = 4.5 Hz), 7.05 and 7.53 (C_6H_4, J_{AB} = 8.3 Hz).

Chlorination of **22** was carried out as described for **16**. Chlorohydrazinium salt **21** (0.11 g, 100%), m.p. 104–105° was obtained from **22** (0.10 g, 0.35 mmol) and t-BuOCl (0.054 g, 0.5 mmol).

2 - (2 - *Methoxycarbonylpropyl*) - 1,1,1 - *trimethylhydrazinium iodide* (**23a**). MeI (4.31 g, 0.03 mol) was added dropwise to **1b** (4.00 g, 0.025 mol) in abs. MeCN (20 ml). After 48 hr at 20° the solvent was evaporated *in vacuo* and the residue was recrystallized from i-PrOH, giving the salt **23a** (6.56 g, 87%), m.p. 162–164°. (Found: C, 31.7; H, 6.4; N, 9.4. $C_8H_{19}N_2O_2I$ requires: C, 31.8; H, 6.3; N, 9.3%.) IR: ν 1715 cm^{-1} (CO), 3430 (NH). ^{1}H-NMR (CD_3OD): δ 1.52 (Me_2C), 3.38 ($Me_3\overset{+}{N}$), 3.80 (MeO).

2 - (2 - *Methoxycarbonylpropyl*) - 1,1,1 - *trimethylhydrazinium chloride* (**23b**). A soln of **23a** (3.02 g, 0.01 mol) in H_2O (10 ml) was passed through an ion-exchange column (d = 1 cm, 22.2 g of Dowex-21K in Cl^- form) and eluted with H_2O. The eluate (85 ml) was evaporated *in vacuo* and the residue was recrystallized from i-PrOH, giving **23b** (1.90 g, 91%), m.p. 152–153°.

1,1,1-*Trimethylhydrazinium tosylate* (**24**). Methyl tosylate (1.86 g, 0.01 mol) in abs MeCN (10 ml) was added dropwise to a cooled (0 to +5°) and stirred soln of DMH (0.60 g, 0.01 mol) in abs. MeCN (15 ml). After 10 hr at 20° the precipitated crystals were filtered off and recrystallized from i-PrOH, providing **24** (2.13 g, 87%), m.p. 219–220°. (Found: C, 48.5; H, 7.5; N, 11.2. $C_{10}H_{18}N_2O_3S$ requires: C, 48.8; H, 7.4; N, 11.4%.) IR: ν 3275 cm^{-1} (NH). UV $\lambda_{max}^{H_2O}$ nm (log ε): 223 (4.13). ^{1}H-NMR (60 MHz, D_2O): δ 2.31 (MeAr), 3.31 ($Me_3\overset{+}{N}$), 7.24 and 7.61 (C_6H_4, J_{AB} = 8.3 Hz).

2-*Chloro*-1,1,1-*trimethylhydrazinium tosylate* (**25**). t-BuOCl (0.13 g, 1.2 mmol) was added to a cooled (−30 to −40°) soln of **24** (0.25 g, 1 mmol) in abs. MeOH (1 ml). After 48 hr at −78° the precipitated salt **25** (0.23 g, 82%), m.p. 104–105°, was filtered off. (Found: C, 43.1; H, 6.0; N, 9.8. $C_{10}H_{17}ClN_2O_3S$ requires: $C_{10}H_{18}N_2O_3S$ requires: C, 48.8; H, 7.4; N, 11.4%.) IR: ν 3275 cm^{-1} (NH). UV $\lambda_{max}^{H_2O}$ nm (log ε): 223 (4.13). ^{1}H-NMR (60 MHz, D_2O): δ 2.31 (MeAr), 3.31 ($Me_3\overset{+}{N}$), 7.24 and 7.61 (C_6H_4, J_{AB} = 8.3 Hz).

REFERENCES

[1] A. B. Zolotoi, O. A. D'yachenko, I. I. Chervin, V. F. Rudchenko, L. O. Atovmyan and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.* in press.

[2] M. A. Shakhgeldiev, O. G. Nabiev, Z. K. Soltanova and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.* in press.

[3a] R. G. Kostyanovsky, V. F. Rudchenko, V. G. Shtamburg, G. V. Shustov and N. B. Tavakalyan, All-Union Conference in Commemoration of A. Ye. Favorsky, Abstracts of papers, p. 125; "Nauka", Leningrad (1980); [b] G. V. Shustov, N. B. Tavakalyan and R. G. Kostyanovsky, XIIth Mendeleev's Congress of General and Applied Chemistry, Abstracts of papers No. 2, p. 13; "Nauka", Moscow (1981); [c] *Idem, Izv. Akad. Nauk SSSR, Ser. Khim.* 1677 (1988).

[4] J. M. Lehn, *Top. Curr. Chem.* **15**, 311 (1970).

[5] H. A. Bent, *Chem. Rev.* **61**, 275 (1961).

[6a] C. C. Levin, *J. Am. Chem. Soc.* **97**, 5649 (1975); [b] N. D. Epiotis, W. R. Cherry, S. Shaik, R. L. Yates and R. E. Bernardi, *Top. Curr. Chem.* **70**, 1 (1977).

[7a] K. Müller, *Helv. Chim. Acta* **53**, 1112 (1970); [b] D. Kost and M. Raban, in *Progress in Theoretical Organic Chemistry* (Edited by I. G. Csizmadia), Vol. 2, p. 20. *Application of MO Theory in Organic Chemistry*. Elsevier, Amsterdam (1977).

[8a] R. G. Kostyanovsky, V. F. Rudchenko, O. A. D'yachenko, I. I. Chervin, A. B. Zolotoi and L. O. Atovmyan, *Tetrahedron* **35**, 213 (1979); [b] G. V. Shustov, A. B. Zolotoi and R. G. Kostyanovsky, *Ibid.* **38**, 2319 (1982); [c] R. G. Kostyanovsky, V. F. Rudchenko, V. G. Shtamburg, I. I. Chervin and Sh. S. Nasibov, *Ibid.* **37**, 4245 (1981).

[9a] W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.* **79**, 572

(1957); [b]S. Hünig, *Helv. Chim. Acta* **54**, 1721 (1971); [c]M. A. Kuznetsov, *Usp. Khim.* **48**, 1054 (1979); [d]S. Wawzonek and W. McKillip, *J. Org. Chem.* **27**, 3946 (1962); [e]M. A. Kuznetsov, *Zh. Org. Khim.* **15**, 1793 (1979).

[10] L. Radom, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **93**, 289 (1971).

[11a] A. V. Pankratov, *The Chemistry of Nitrogen Fluorides*. "Khimiya" (1973); [b]A. V. Fokin, Yu. N. Studnev and L. D. Kuznetsova, in *Reactions and Methods of Investigating Organic Compounds*. "Khimiya", Vol. 24 (1976); [c]J. A. Gervasi, M. Brown and L. A. Bigelow, *J. Am. Chem. Soc.* **78**, 1679 (1956); [d]F. P. Avonda, J. A. Gervasi and L. A. Bigelow, *Ibid.* **78**, 2798 (1956); [e]J. W. Fraser, *J. Inorg. Nucl. Chem.* **16**, 63 (1969); [f]N. F. Smith, J. A. Castellano and D. D. Perry, in *Modern Chemistry of Propellants*, p. 163. Atomizdat (1972).

[12a] R. A. Mitsch, *J. Org. Chem.* **33**, 1847 (1968); [b]W. C. Firth, *Ibid.* **33**, 3489 (1968).

[13a] J. K. Ruff, *Inorg. Chem.* **5**, 1791 (1966); [b]A. R. Young and D. Moy, *Ibid.* **6**, 178 (1967).

[14a] Y. Shvo, in *The Chemistry of the Hydrazo, Azo and Azoxy Groups* (Edited by S. Patai), Part 2, p. 1017. Wiley (1975). [b]I. D. Kalikhman, E. N. Medvedeva, P. V. Makerov and V. A. Lopyrev, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2662 (1980).

[15a] W. Oppolzer and H. P. Weber, *Tetrahedron Lett.* 1711 (1972); [b]W. Oppolzer, *Ibid.* 2199 (1970); [c]H. Dorn and H. Dilcher, *Liebigs Ann. Chem.* **717**, 104 (1968).

[16] H. G. Viehe, R. Merenyi, L. Stella and Z. Janousek, *Angew. Chem. Int. Ed. Engl.* **18**, 917 (1979).

[17] G. V. Shustov, N. B. Tavakalyan, L. L. Shustova, A. P. Pleshkova and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.* 364 (1982).

[18] M. I. Bruce, B. L. Goodall and F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* 1651 (1975).

[19a] R. T. Sanderson, *Chemical Bonds and Bond Energy*, p. 36. Academic Press, New York (1976); [b]E. Allenstein, *Z. Anorg. Allgem. Chem.* **308**, 3 (1961); [c]H. Lumbroso, *Bull. Soc. Chim. Fr.* 2519 (1963).

[20a] P. Kovacic, M. K. Lowery and K. W. Field, *Chem. Rev.* **70**, 639 (1970); [b]E. Schmitz, *Usp. Khim.* **45**, 54 (1976); [c]L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Vol. 1, p. 139, Vol. 6, p. 115. Wiley, New York (1967), (1977).

[21] W. Oppolzer, *Tetrahedron Lett.* 1707 (1972).

[22] V. Rautenstrauch, *J. Chem. Soc. Chem. Commun.* 1122 (1969).

[23] H. Ripperger, K. Schreiber and G. Snatzke, *Tetrahedron* **21**, 727 (1965).

[24] R. G. Kostyanovsky, V. I. Markov and I. M. Gella, *Tetrahedron Lett.* 1301 (1972).

[25a] E. Nagy-Felsobuki and J. B. Peel, *J. Chem. Soc. Faraday Trans. II*, 1927 (1978); [b]F. Carnovale, T. H. Gan and J. B. Peel, *Aust. J. Chem.* **32**, 719 (1979).

[26] R. L. Hinman, *J. Am. Chem. Soc.* **78**, 1645 (1965).

[27] P. Hope and L. A. Wiles, *J. Chem. Soc.* (C) 2636 (1967).

[28a] E. E. Mikhlina, K. F. Turchin, N. A. Komarova and M. V. Rubtsov, *Chim. Heterocikl. Soed.* 259 (1966); [b]S. F. Nelsen, P. M. Gannet and D. J. Steffek, *J. Org. Chem.* **45**, 3857 (1980).