Diazepinones from Sydnones and Isopropylidenecyclobutenone. Extension of the Frontier Molecular Orbital Model for Sydnone Cycloadditions[1)]

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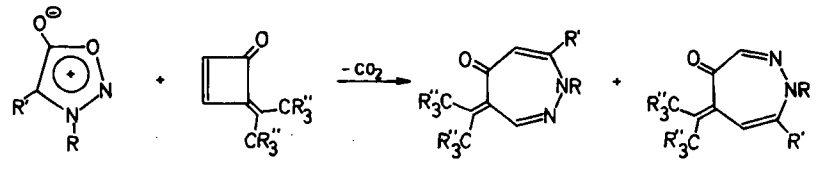
On heating the sydnones **1a–h** with isopropylidenecyclobutenone (**2**) in refluxing toluene dihydrodiazepin-5-ones (**3a–h**) are obtained in the case of *N*-phenyl- and dialkylsydnones. The *N*-alkyl-*C*-hydrogensydnones, however, yield two regioisomeric products, the dihydrodiazepin-5-ones **3d,e** as well as the corresponding diazepin-4-ones **4d,e**. The frontier molecular orbital model, as applied to sydnones, is critically examined. Extension of the simple model to the calculation of selected encounter complexes is presented. In this way not only the preferred formation of diazepin-5-ones (**3**) is correctly predicted but the ratio of **3**:**4** is also satisfactorily reproduced. *X*-ray diffraction has been used to determine the structure of **4d** which is between a boat and a chair and shows a very short NN single bond.

Diazepinone aus Sydnonen und Isopropylidencyclobutenon. Erweiterung des Grenzorbitalmodells für Sydnon-Cycloadditionen[1)]

Beim Erhitzen der Sydnone **1a–h** mit Isopropylidencyclobutenon (**2**) in siedendem Toluol werden im Fall der *N*-Phenyl- und Dialkylsydnone Dihydrodiazepin-5-one **3a–h** erhalten. Die *N*-Alkyl-*C*-Wasserstoff-Sydnone ergeben jedoch zwei regioisomere Produkte, sowohl die Dihydrodiazepin-5-one **3d,e** als auch die entsprechenden Diazepin-4-one **4d,e**. Das Grenzorbitalmodell wird in seiner Anwendung auf Sydnon-Additionen kritisch überprüft. Es wird eine Erweiterung des einfachen Modells vorgestellt, die die Berechnung von Begegnungskomplexen zum Ziel hat. Auf diese Weise wird nicht nur die bevorzugte Bildung von Diazepin-5-onen (**3**) korrekt vorhergesagt, auch das Verhältnis von **3**:**4** wird befriedigend reproduziert. Durch Röntgenbeugung wird die Struktur von **4d** ermittelt, die zwischen Wanne und Sessel liegt und eine sehr kurze NN-Einfachbindung aufweist.

1,3-Dipolar cycloadditions with cyclobutenes provide access to seven-membered heterocycles. With diazoalkanes[1,2,3)], münchnones[2,4,5)], and nitrile ylides[5)], resp., dihydrodiazepines and dihydroazepines can be synthesized. Whereas the synthesis of six-membered heterocycles from mesoionic compounds has been investigated[6,7)], only one example of an addition of a sydnone ring to a derivative of cyclobutene has so far been described: in the reaction of *N*-phenylsydnone with cyclooctatetraene Padwa and Lim[8a)] isolated a by-product whose formation can be interpreted as an addition to the valence tautomer bicyclooctatriene. At present Regitz et al. are synthesizing diazepines by adding sydnones to tri-*tert*-butyl(*tert*-butoxycarbonyl)cyclobutadiene[8b)]. We now report on the cycloaddition of the sydnones **1a–h** to isopropylidenecyclobutenone (**2**) (Scheme 1).

Scheme 1



	R	R'
a	C_6H_5	CH_3
b	C_6H_5	H
c	C_6H_5	Cl
d	CH_3	H
e	$C_6H_5CH_2$	H
f	CH_3	CH_3
g	$-(CH_2)_4-$	
h	$-(CH_2)_3-$	

	R''
a	H
b	D

	R	R'	R''
a	C_6H_5	CH_3	H
b	C_6H_5	H	H
c	C_6H_5	Cl	H
d	CH_3	H	H
e	$C_6H_5CH_2$	H	H
f	CH_3	CH_3	H
g	$-(CH_2)_4-$		H
h	$-(CH_2)_3-$		H
i	CH_3	CH_3	D
j	$-(CH_2)_4-$		D

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Results

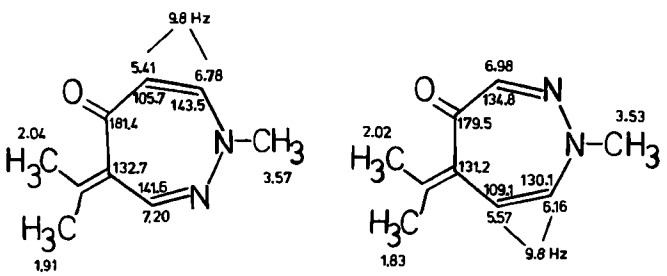
One of the reasons for the lack of reported cyclobutene to sydnone additions certainly is the low dipolar reactivity of the sydnones, the reaction requiring higher temperatures and a longer period of time. Under these conditions, the cleavage of the cyclobutene ring considerably competes with the dipolar cycloaddition. The cleavage of the cyclobutenone ring leads to a traceable vinyl ketene. The reaction rate of the ring opening of alkyl- or aryl-substituted cyclobutenones at 100°C is so large[9,10] that there is hardly any chance of a successful reaction with sydnones. At room temperature pure isopropylidenecyclobutenone (**2a**)[11] is a lachrymatory liquid with a pungent smell, which solidifies to an opaque glassy substance insoluble in acetone. However, its stability in solution is enormous compared with other cyclobutenones. At −30°C it can be stored in solution for an unlimited time, at room temperature in ether it is stable for several months. In boiling toluene the half-life of **2a** amounts to ca. one day and in boiling xylene to about two hours. This considerable stability at higher temperatures is the basis for the cycloaddition chemistry of **2a**.

Typical conditions for the reactions with sydnones are heating of **2a** and the dipole in refluxing toluene for several hours (1 − 5 h). The *N*-phenylsydnones **1a**−**c** react with **2a** to yield one single regioisomer, the dihydrodiazepin-5-ones (**3a**−**c**). Both neat and in solution, these isomers show a light yellow colour, caused by an absorption band at about 340 nm. The dialkyl sydnones **1f**−**h** react in an analogous way. (Purity control by TLC allows to conclude that a trace of the regioisomer **4f**−**h** might have been formed.)

The *N*-alkyl-*C*-hydrogensydnones **1d**, **e** require longer reaction times (17 and 29 h, resp.) because of their lower reactivity. The result was surprising. The formation of two products with similar retention times could clearly be perceived (GC, TLC). The isomeric diazepin-5-ones and diazepin-4-ones are formed in a ratio of about 4:3, which means that the regioselectivity already observed with the other sydnones also predominates in these cases. In contrast to the 5-oxo isomers the 4-oxo isomers show a reddish colour in the solid state and an intense yellow colour in solution ($\lambda_{max} \approx 410$ nm).

Since by diazoalkane addition to **2a** only NH-diazepin-4-ones are available[1,3], the described syntheses of both diazepin-5-ones **3** and *N*-alkyldiazepine-4-ones **4** represent a valuable extension of the diazepine syntheses known so far.

Scheme 2



3d **4d**

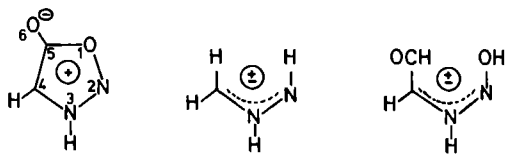
The characteristic differences in the ^{1}H-NMR spectra of the two regioisomers are discussed for the compounds **3d** and **4d** (Scheme 2).

The significant differences involve the two olefinic CH units and the azomethine group. The carbonyl-isopropylidene fragment displays remarkably constant resonances. The stronger polarization of the CH=CH unit in the diazepin-5-ones is expressed both in the ^{1}H and in the ^{13}C spectra. A further diagnostic aid for differentiating the two regioisomers is the line width of the azomethine proton: due to ^5J coupling with the methyl groups the band is broader in **3** than in **4**.

Frontier Orbital Data of Sydnones

With one exception[12] known to us the properties of the frontier orbitals of sydnones have not yet been published in spite of numerous theoretical investigations[13]. Since our results for the parent compound **5** deviate significantly from the values given in Lit.[12], various sydnones have been calculated with four different methods (MNDO[14], MINDO/3[15], CNDO/2[16], ab initio STO-3G[17]). The geometry of **5** has been optimized with the help of MNDO and MINDO/3 methods and shows good agreement with the experimental data of (*p*-bromophenyl)sydnone[18] and 4,4′-dichloro-3,3′-ethylenebissydnone[19] (MINDO/3: O1−N2 135.3, N2−N3 125.2, N3−C4 133.4, C4−C5 144.9, C5−O1 137.0, C5−O6 121.8 pm). In Table 1 the charge distribution and dipole moments calculated in this work are compared with literature data.

Scheme 3



5 **6** **7**

All calculations clearly indicate the polarization of the carbonyl group. The ring oxygen atom shows a negative partial charge. The two atoms N-2 and C-4 involved in the dipolar cycloaddition deserve special attention. In contrast to ref.[12] N-2 turns out to be only weakly negative or positively charged, whereas C-4 represents the negative end of the dipole.

In order to recognize the azomethine character of the sydnone, which has particularly been pointed out by Houk et al.[20], the frontier orbitals of **5** were compared with those of the azomethine imine **6** and the 3-formyl-1-hydroxy derivative **7**. All four MO methods lead to indentical statements with respect to the density distribution of the HOMO and LUMO. In addition, the substituent effect on **6** is described in the same way and the 3-formyl-1-hydroxy-azomethine imine simulates the sydnone **5** correctly. Due to the similarity of the results it is sufficient to give only the MINDO/3 coefficients, for example: **5**, ε_{LU} = 0.37 eV (C −0.44, N 0.62, N −0.56), ε_{HO} = −8.48 eV (C −0.66, N

Table 1. Comparison of charge distribution and dipole moments (in Debye) calculated in this work with literature data

Method	q_1	q_2	q_3	q_4	q_5	q_6	μ	Lit.
MNDO	−0.14	−0.03	−0.01	−0.24	0.33	−0.26	5.57	this work
MINDO/3	−0.38	0.07	0.34	−0.40	0.79	−0.56	6.35	this work
CNDO/2	−0.11	0.04	0.12	−0.18	0.37	−0.43	7.85	this work
ab initio	−0.14	0.01	−0.15	−0.07	0.29	−0.30	5.37	this work
MINDO/3		−0.16		−0.02				[12]
ab initio	−0.22	0.18	−0.34	−0.25	0.40	−0.42	5.68	[13]

Table 2. Frontier orbital data for the sydnones **1a–d,f**, the *N*-*tert*-butyl- and *N*-(2,6-dimethylphenyl)-*C*-methyl derivative. Optimization by means of the respective method, for STO-3G with MNDO

			MNDO				MINDO/3				CNDO/2				GAUSSIAN 80 (STO-3G)			
	N-R	C-R	E/eV	C	N	N	E/eV	C	N	N	E/eV	C	N	N	E/au	C	N	N
5	H	H	-1.01	+0.48	-0.55	+0.59	+0.37	-0.44	+0.62	-0.56	+1.40	-0.31	+0.57	-0.65	+0.184	-0.46	+0.64	-0.71
			-9.15	-0.67	+0.03	+0.55	-8.48	-0.66	+0.03	+0.59	-10.07	-0.57	+0.11	+0.41	-0.202	-0.64	+0.08	+0.51
1d	CH_3	H	-0.90	+0.47	-0.54	+0.59	+0.40	+0.42	-0.59	+0.56	+1.49	+0.30	-0.55	+0.63	+0.191	-0.45	+0.64	-0.71
			-8.96	-0.67	+0.03	+0.55	-8.27	-0.67	+0.03	+0.57	-9.87	+0.57	-0.11	-0.41	-0.194	-0.64	+0.09	+0.50
	$C(CH_3)_3$	H	-0.71	-0.47	+0.55	-0.58	+0.61	+0.41	-0.60	+0.56	+2.00	-0.30	+0.58	-0.63	+0.194	-0.45	+0.64	-0.69
			-8.83	+0.67	-0.03	-0.55	-8.07	+0.67	-0.04	-0.58	-9.58	-0.56	+0.12	+0.43	-0.184	+0.63	-0.11	-0.52
1f	CH_3	CH_3	-0.94	-0.47	+0.54	-0.58	+0.35	+0.41	-0.59	+0.56	+1.45	-0.30	+0.55	-0.63	+0.197	+0.45	-0.64	+0.70
			-8.89	-0.66	+0.01	+0.54	-8.04	-0.66	+0.03	+0.35	-9.36	-0.56	+0.06	+0.43	-0.181	+0.63	-0.05	-0.51
1b	C_6H_5	H	-0.62	+0.36	-0.44	+0.45	+0.68	-0.41	+0.61	-0.56	+3.42	+0.14	-0.41	+0.34	+0.183	+0.39	-0.51	+0.60
			-1.04	+0.31	-0.32	+0.37					+1.13	+0.26	-0.41	+0.53				
			-8.87	-0.67	+0.03	+0.55	-8.08	+0.67	-0.03	-0.58	-9.61	-0.56	+0.12	+0.41	-0.191	+0.64	-0.09	-0.50
1a	C_6H_5	CH_3	-0.76	-0.37	+0.44	-0.47	+0.62	+0.40	-0.60	+0.56	+2.97	-0.11	+0.30	-0.26	+0.195	-0.42	+0.57	-0.65
			-0.92	-0.30	-0.32	+0.35					+1.47	-0.27	+0.46	-0.55				
			-8.79	-0.66	+0.01	+0.54	-7.87	+0.66	-0.01	-0.56	-9.15	-0.56	+0.06	+0.43	-0.178	-0.63	+0.05	+0.51
	2,6-Dimethylphenyl	CH_3	-0.75	+0.30	-0.36	+0.38	+0.65	-0.40	+0.60	-0.57	+1.93	+0.30	-0.57	+0.62	+0.199	+0.47	-0.62	+0.69
			-0.84	+0.36	-0.42	+0.45												
			-8.78	+0.67	-0.01	-0.54	-7.84	-0.66	+0.01	+0.55	-9.12	-0.56	+0.06	+0.43	-0.176	+0.63	-0.06	-0.51
1c	C_6H_5	Cl	-0.88	-0.20	+0.26	-0.27	+0.42	-0.08	+0.11	-0.11					+0.171	+0.43	-0.61	+0.69
			-1.15	+0.41	-0.48	+0.53	+0.38	-0.43	+0.58	-0.52								
			-9.06	+0.66	-0.02	-0.53	-8.06	+0.63	-0.05	-0.58					-0.204	+0.63	-0.07	-0.49

0.03, N 0.59); **6**, ε_{LU} = 1.55 eV (C −0.60, N 0.67, N −0.44), ε_{HO} = −7.92 eV (C 0.67, N 0.11, N −0.74); **7**, ε_{LU} = 0.24 eV (C −0.32, N 0.63, N −0.55), ε_{HO} = −8.26 eV (C −0.70, N 0.01, N 0.57).

When comparing the data for **5** with those from ref.[12], a distinct contradiction is observed (**5**[12]: ε_{LU} = 1.18 eV (C-4 0.56, N-2 0.37), ε_{HO} = −8.48 eV (C-4 −0.65, N-2 0.66)).

The model calculations carried out here for **5**–**7** show that the sydnone **5** is to be considered as an azomethine imine with an electron withdrawing substituent at the terminal C and an electron donating substituent at the terminal N atom.

In order to ascertain further substituent effects, MO calculations with sydnone derivatives were carried out. The geometry optimization was effected with the respective method, for ab initio STO-3G with MNDO. The results in Table. 2 show that the substituent effect on the sydnone system remains very small. The first ionization energy[13] of

N-methylsydnone (**1d**), obtained PE spectroscopically ($IE_{1,V}$ = 8.9 eV), is satisfactorily reproduced. No substituent influence on the frontier orbital coefficients is observable. Only *N*-aryl substitution causes a splitting of the frontier orbitals which leads to two orbitals lying close together and showing comparable coefficients in the LUMO.

Regioselectivity of the Sydnone Addition

In the literature[20–22] and especially in textbooks[23] the discussion of regioselectivity is unsatisfactory. This holds true, above all, for the problem of the controlling pair of frontier orbitals. The sydnone addition is largely considered as a sydnone-LUMO controlled reaction. Obviously, this assumption follows from a neglect of the O-donor function at the terminal N of the sydnone. When calculating the frontier orbital energies of different classes of dipolarophiles the correlations compiled in Fig. 1 are obtained similar to the procedure of Houk et al.[21].

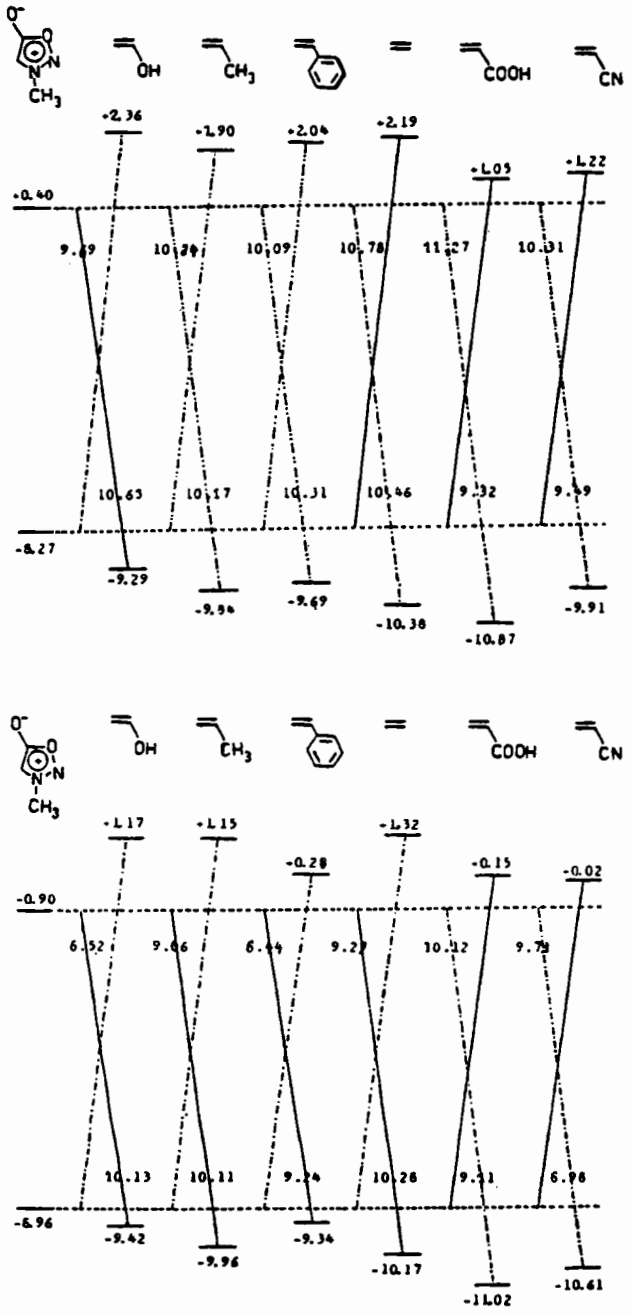


Fig. 1. Correlations of the frontier orbital interactions of *N*-methylsydnone (**1d**) with olefinic dipolarophiles (above: MINDO/3, below: MNDO)

According to both MNDO and MINDO/3 it follows that the reaction of sydnones with (*Z*)-olefins is HOMO dipole controlled in good agreement with chemical experience. Singly *Z*-substituted dipolarophiles favourably add *Z*-substituents at the terminal N of the azomethine fragments[12,24]. The frontier orbital scheme in Fig. 2a was consulted for an explanation. The preference of the 3-position for *Z* in the pyrazolines and pyrazoles, resp., only would be understandable when unjustifiably presuming a sydnone-LUMO control. However, the addition of *Z*-dipolarophiles can easily be interpreted on the basis of a sydnone-HOMO control with the data given in Table 2 and Fig. 2b. Yet, the regioselectivity of the addition to 1,2-*Z*,*C*-substituted dipolarophiles (e.g. *trans*-cinnamic ester) cannot be explained with the help of Fig. 2b, as is shown by MNDO, MINDO/3, and CNDO/2 calculations.

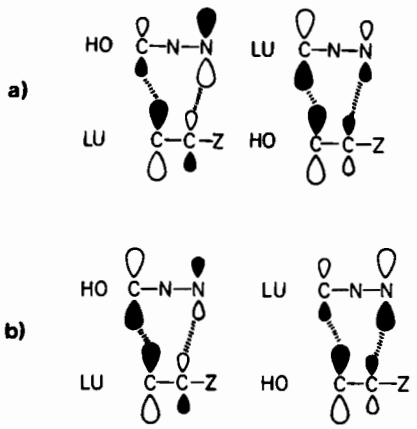


Fig. 2. a) Frontier orbital scheme with sydnone-LUMO control according to ref.[22,23].
b) Frontier orbital scheme derived in this work with a reversed polarization of sydnone (**5**). Sydnone-HOMO control is predicted for (*Z*)-olefins

Should this result argue for the just dismissed polarization according to Fig. 2a? We believe, that the problem can only be solved by extending the frontier orbital model of Fig. 2b and not by returning to the incorrect model of Fig. 2a. Huisgen et al.[25a] considered an approach of the two reactants in parallel planes. During the presumably concerted approach of the terminal atoms of the 1,3-dipole to the dipolarophile noticeable overlap occurs on the way to the transition state. Thereby, especially the O1–N2 and the C4–C5 bonds, resp., of the sydnone are stretched already in the transition state.

Proceeding from the experimental geometry of *N*-(*p*-bromophenyl)sydnone[18] and lengthening the two distances stretched in Scheme 4 by identical amounts leads to a result unexpected in its magnitude (Tab. 3). An equalization of the terminal frontier orbital coefficients results from a mere

stretching of 5 pm whereas a stretching of 10 pm leads to a complete inversion of the polarization.

Scheme 4

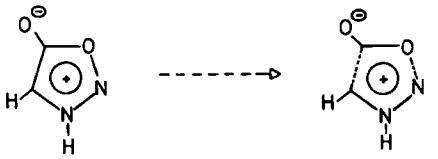
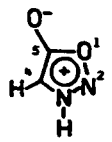


Table 3. Influence of an extension of the O1–N2 and C4–C5 bonds, resp., on the frontier orbital polarization according to MNDO

Extension / Å	HOMO E/eV	HOMO C_4	HOMO N_2	LUMO E/eV	LUMO C_4	LUMO N_2
0.00	-9.29	+0.65	-0.58	-1.27	+0.49	+0.57
+0.05	-9.33	+0.64	-0.62	-1.27	+0.53	+0.54
+0.10	-9.37	+0.63	-0.66	-1.26	+0.57	+0.52
+0.15	-9.41	+0.62	-0.68	-1.25	+0.60	+0.50
+0.20	-9.45	+0.61	-0.71	-1.23	+0.63	+0.48
+0.30	-9.54	+0.58	-0.75	-1.20	+0.68	-0.42



Similar calculations have been carried out for the münchnone system. However, according to CNDO/2, the inversion of the polarization in that molecule requires a stretching of 30 pm[25b].

As a consequence of these considerations, it may depend on the relative position of the transition state on the reaction coordinate which of the regioisomers is formed preferably. If the transition state is located early, as for the more reactive singly *Z*-substituted dipolarophiles, a regioselectivity corresponding to that of the uninfluenced sydnone will be found. However, if the position of the transition state is close to the products, as for the derivatives of cinnamic acid, the inversion of the coefficients influences product formation.

Application of the simple frontier orbital model of Fig. 2b to the cycloaddition of the sydnones to isopropylidenecyclobutenone (**2**) does not explain the preferred formation of the diazepin-5-ones. Fig. 3 shows that both MNDO and STO-3G methods produce incorrect predictions for this type-II addition.

Therefore it is possible that the transition state of the 1,3-dipolar cycloaddition of sydnones to cyclobutenone **2** is located relatively late and that the favoured regioisomerism is not determined before the two reactants are tightly assoziated. That means, that with the help of MO calculations for encounter complexes information on the relative stabilities of both orientations can be obtained. According to Huisgen et al.[25a] we may assume an approach of the reactants in two parallel planes. In Fig. 4 four conceivable encounter complexes are depicted for the addition of sydnones to cyclobutenone **2**. For the MO calculations MNDO geometries were used. The centres of the two axes C=C of **2** and C4–N2 of **5** are lying one on top of the other. The approach of the reactants was simulated by means of the distance between these centres.

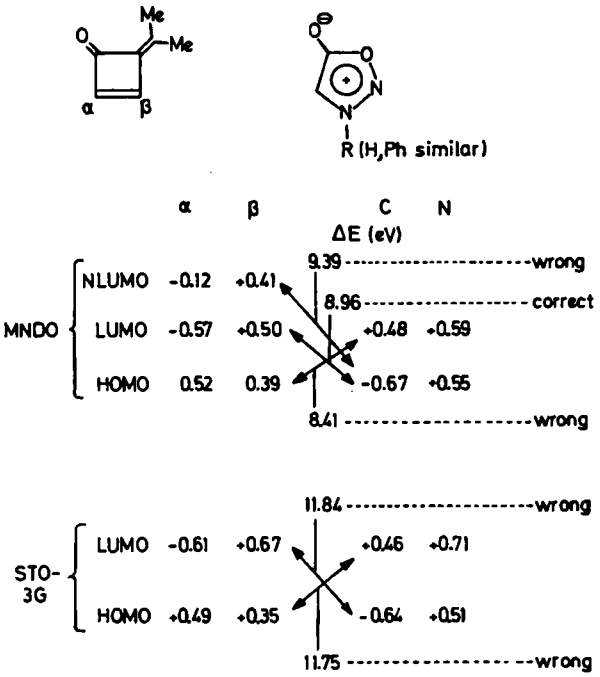


Fig. 3. Application of the simple frontier orbital model to the sydnone-isopropylidenecyclobutenone addition (MNDO and STO-3G methods). The orientation chosen (N atom of sydnone to C-β of **2**) corresponds to the formation of the main product **3**

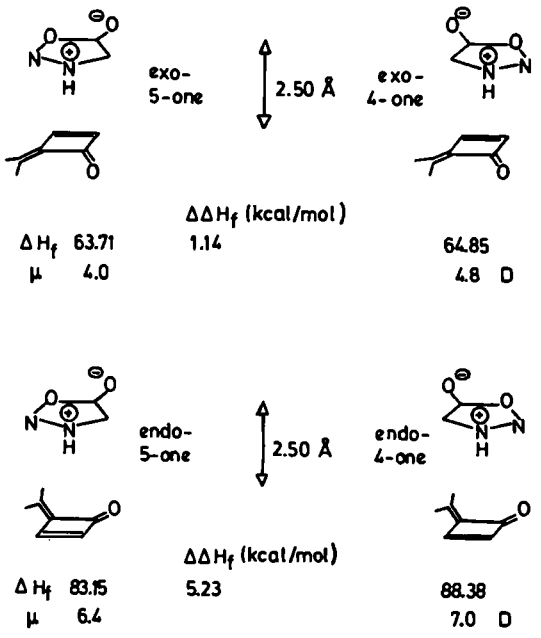


Fig. 4. Four different encounter complexes between sydnone (**5**) and cyclobutenone **2**. Energies according to MNDO in kcal/mol. Distance 250 pm. Dipole moments in D

With this intermolecular model it is possible to make the following statements:

1. The *exo* orientation is clearly favoured over the *endo* arrangement,

2. the less stable *endo* complexes possess larger dipole moments,

3. the complexes leading to diazepin-5-ones have a lower energy than the corresponding arrangements which yield diazepin-4-ones. The calculated difference in energy of 1.14 kcal/mol corresponds to a product ratio of about 87:13.

Crystal Structure of 4d[26]

The molecule (Figures 5,6) is in a general position of the crystal structure. The N–N single bond (Table 5) is the shortest one of comparable 1,2-diazepines of which the crystal structures are published[27]. A similarly short bond (and total molecular geometry) was found in the analogous compound with an H atom instead of the methyl group at the N(1) atom[26]. The N–N bond is part of a conjugative system, which extends from the atom N(2) around the longer part of the ring to the atom C(6), as indicated by a general shortening of all the single and lengthening of the double bonds in this part of the molecule. There is no significant evidence of this kind for conjugative interactions in the rest of the molecule. The ring conformation is about halfway between a boat and a chair with the mirror symmetry of both forms approximately present, across the vertical plane through the atom C(3) and the midpoint of the N(1)–N(2) bond. The torsional angles N(2)–C(1)–C(2)–O and O–C(2)–C(3)–C(6), in both of which the C(2)–O bond is involved, are 164.3(2) and 38.4(3)°, respectively. – None of the intermolecular distances is unusually short.

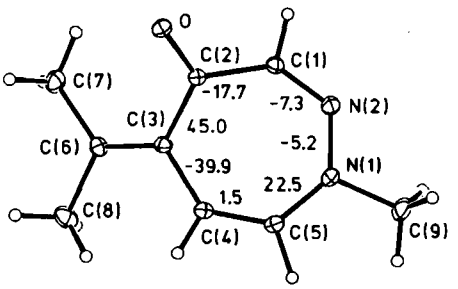


Fig. 5. Molecule of **4d** with atomic thermal vibration ellipsoids (25% probability, H atoms of arbitrary size) and torsional angles around the seven-membered ring (e. s. d.'s 0.2–0.3°)

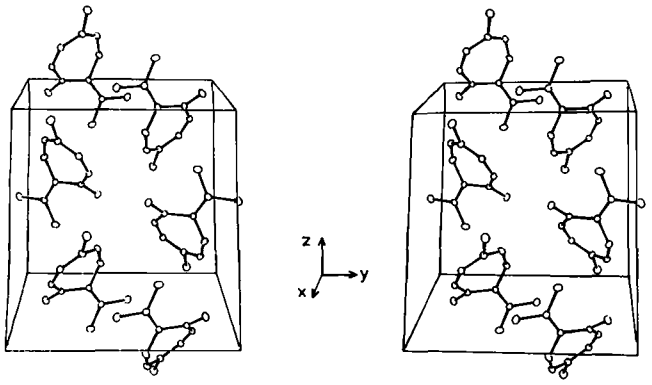


Fig. 6. Stereoscopic view of the molecular packing in **4d** with unit cell (H atoms omitted for clarity)

Table 4. Data of crystallography, diffractometry, and refinement for **4d**

Crystal system monoclinic, a = 834.2(4), b = 1067.5(5), c = 1131.4(6) pm, β = 117.27(3)°, V = 895.5 · 10^6 pm^3, space group $P2_1/c$, Z = 4, $d_{calc.}$ = 1.218 mg · mm^{-3}, measuring temperature T = −130°C, $2\Theta_{max}$ (Mo-K_α) 67°, independent reflections observed ($\lvert F_o \rvert \geq 3.92\sigma_F$) 2953, total 3447, varied parameters 139, R obsd., total 0.062; 0.074, R_w obsd., total 0.106; 0.107, residual el. density −0.38 ··· 0.43 · 10^{-6} e · pm^{-6} (min ··· max)

Table 5. Bond lengths (pm) and bond angles (deg.) between non-H atoms in **4d**

Bond		Bond angle	
C(1)-C(2)	148.0(2)	C(1)-C(2)-C(3)	120.8(1)
C(2)-C(3)	149.0(2)	C(2)-C(3)-C(4)	114.4(1)
C(3)-C(4)	146.1(2)	C(3)-C(4)-C(5)	130.2(2)
C(4)-C(5)	134.3(2)	C(4)-C(5)-N(1)	129.5(2)
C(5)-N(1)	138.9(2)	C(5)-N(1)-N(2)	127.8(1)
N(1)-N(2)	133.4(2)	N(1)-N(2)-C(1)	125.5(1)
N(2)-C(1)	130.2(2)	N(2)-C(1)-C(2)	135.3(1)
O-C(2)	123.2(2)	O-C(2)-C(1)	116.9(1)
		O-C(2)-C(3)	122.3(1)
C(6)-C(3)	135.4(2)	C(6)-C(3)-C(2)	123.4(1)
		C(6)-C(3)-C(4)	122.1(1)
C(7)-C(6)	150.0(2)	C(7)-C(6)-C(3)	124.7(1)
C(8)-C(6)	150.6(2)	C(8)-C(6)-C(3)	121.2(1)
		C(7)-C(6)-C(8)	114.0(1)
C(9)-N(1)	146.3(2)	C(9)-N(1)-N(2)	113.7(1)
		C(9)-N(1)-C(5)	117.9(1)

Conclusion

We summarize that the correct frontier orbital model of Fig. 2b with HOMO dipole control does not yet allow a satisfactory prediction of the regioselectivity of the cycloaddition of sydnones to isopropylidenecyclobutenone (**2**) (though that scheme applies satisfactorily to other (*Z*)-olefins). This failure may be attributed both to a large structural reorganization of the sydnone in the transition state and to the contribution of further orbital interactions and presumably also of nonbonded contacts. However, the SCF-calculation of encounter complexes with distances reasonable for transition states (250 pm) allows better predictions.

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Experimental

Melting points: Büchi 510 melting point apparatus, uncorrected. – ^{1}H NMR: Varian EM-360, Bruker WP 80. – ^{13}C NMR: Varian XL-100. – MS: Varian MAT CH 5. – IR: Spectrometer 297 Perkin-Elmer. – UV: Spectrometer M 4 Q III Carl Zeiss.

Syntheses of 1,4-Dihydro-5H-1,2-diazepin-5-ones (**3a–j**) *and of 1,5-Dihydro-4H-1,2-diazepin-4-ones* (**4d,e**): Sydnones **1a–h**[28] and isopropylidenecyclobutenone (**2**)[11] were refluxed in dry toluene to the exclusion of moisture. Reactions were completed when **2** could not be identified by GC. Details in Table 6.

Table 6. Preparation of diazepin-5-ones **3a–j** and of diazepin-4-ones **4d,e**

Sydnone **1** g (mmol)	Cyclobutenone **2** g (mmol)	Toluene ml	Time h	Diazepin-5-one **3** [Diazepin-4-one **4**] m.p. (°C)/%	Formula (Mol. Weight) [M^+, MS] Analysis (C, H, N)
a: 0.94 (5.36)	**a**: 0.58 (5.36)	50	1.5	**a**: 129–130/43	$C_{15}H_{16}N_2O$ (240.3) [240] Calcd. 74.97 6.71 11.66 Found 74.71 6.87 11.61
b: 0.90 (5.50)	**a**: 0.59 (5.45)	60	3.5	**b**: 103/52	$C_{14}H_{14}N_2O$ (226.3) [226] Calcd. 74.31 6.24 12.38 Found 74.48 6.36 12.10
c: 0.88 (4.47)	**a**: 0.49 (4.53)	15	1.35	**c**: 89/32	$C_{14}H_{13}ClN_2O$ (260.7) [260 (^{35}Cl)] Calcd. 64.50 5.03 10.74 Found 64.39 5.00 10.51
d: 1.45 (14.5)	**a**: 0.59 (5.45)	20	17	**d**: 65/38	$C_9H_{12}N_2O$ (164.2) [164] Calcd. 65.83 7.37 17.06 Found 65.65 7.44 16.75
				[ca. 20/27]	$C_9H_{12}N_2O$ (164.2) [164] Calcd. 65.83 7.37 17.06 Found 65.51 7.49 16.76
e: 0.99 (5.62)	**a**: 0.62 (5.73)	25	29	**e**: 65–66/28	$C_{15}H_{16}N_2O$ (240.3) [240] Calcd. 74.97 6.71 11.66 Found 74.77 6.81 11.47
				[54/19]	$C_{15}H_{16}N_2O$ (240.3) [240] Calcd. 74.97 6.71 11.66 Found 74.57 6.81 11.60
f: 0.69 (6.05)	**a**: 0.59 (5.45)	15	3.75	**f**: 144/26 [-/Traces]	$C_{10}H_{14}N_2O$ (178.2) [178] Calcd. 67.39 7.92 15.72 Found 66.95 7.99 15.57
g: 0.76 (5.45)	**a**: 0.59 (5.45)	10	4.5	**g**: 120–121/37 [-/Traces]	$C_{12}H_{16}N_2O$ (204.3) [204] Calcd. 70.56 7.90 13.71 Found 70.24 7.86 13.52
h: 0.75 (5.95)	**a**: 0.63 (5.82)	15	9	**h**: 142/46 [-/Traces]	$C_{11}H_{14}N_2O$ (190.2) [190] Calcd. 69.45 7.42 14.72 Found 69.49 7.44 14.74
f: 0.80 (7.01)	**b**: 0.85 (7.21)	15	3.75	**i**: 144–145/29 [-/Traces]	$C_{10}H_8D_6N_2O$ (184.3)
g: 0.95 (6.77)	**b**: 0.76 (6.65)	15	4.5	**j**: 121–122/43 [-/Traces]	$C_{12}H_{10}D_6N_2O$ (210.3)

Isolation and Purification

1,4-Dihydro-4-isopropylidene-7-methyl-1-phenyl-5H-1,2-diazepin-5-one (**3a**): The mixture was evaporated to dryness in vacuo and the residue was digested with 3 ml of ether. The brown solid was crystallized from little ethyl acetate to give light yellow needles. – IR (KBr): 1630 cm^{-1} (C=O). – UV ($CHCl_3$): λ_{max} (lg ε) = 308 (4.14), 360 nm (4.30). – ^1H NMR ($CDCl_3$): δ = 1.92 (s; 6H, 7-CH_3, *anti*-CH_3), 2.14 (s; 3H, *syn*-CH_3), 5.66 (s; 1H, 6-H), 7.50 (mc; 6H, 3-H and C_6H_5). – ^{13}C NMR ($CDCl_3$)): δ = 21.3 (q; *anti*-CH_3), 22.0 (q; *syn*-CH_3), 25.5 (q; 7-CH_3), 110.2 (d; C-6), 125.9 (d; C_6H_5, 2*o*-C), 127.4 (d; C_6H_5, *p*-C), 129.0 (d; C_6H_5, 2*m*-C), 131.6 (s; C-4), 143.5 (d; C-3), 144.3 (s; C_6H_5, *ipso*-C), 144.9 (s; $C(CH_3)_2$), 151.9 (s; C-7), 181.3 (s; C-5). – MS (70 eV): *m/z* = 240 (95%, M^+), 225 (30, M – CH_3), 149 (23, M – C_6H_5N), 77 (100, C_6H_5).

1,4-Dihydro-4-isopropylidene-1-phenyl-5H-1,2-diazepin-5-one (**3b**): The mixture was evaporated to dryness in vacuo. The residual material was digested in 10 ml of ether. The precipitated sydnone **1b** was removed by filtration. The filtrate yields light yellow needles at –10°C within 24 h. The material was recrystallized from ethyl acetate. – IR (KBr): 1632 cm^{-1} (C=O). – UV ($CHCl_3$): λ_{max} (lg ε) = 312 (3.91), 365 nm (3.67). – ^1H NMR ($CDCl_3$): δ = 1.93 (s; 3H, *anti*-CH_3), 2.11 (s; 3H, *syn*-CH_3), 5.67 (d, *J* = 9.8 Hz; 1H, 6-H), 7.23 (d, *J* = 9.8 Hz; 1H, 7-H), 7.30–7.63 (m; 6H, 3-H and C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (q; *anti*-CH_3), 22.2 (q; *syn*-CH_3), 108.9 (d; C-6), 119.5 (d; C_6H_5, 2*o*-C), 125.6 (d; C_6H_5, *p*-C), 129.9 (d; C_6H_5, 2*m*-C), 132.5 (s; C-4), 140.8 (d; C-7), 143.2 (d; C-3), 144.5 (s; $C(CH_3)_2$), 146.0 (s; C_6H_5, *ipso*-C), 181.5 (s; C-5). – MS (70 eV): *m/z* = 226 (100%, M^+), 211 (14, M – CH_3), 135 (32, M – C_6H_5N), 77 (88, C_6H_5).

7-Chloro-1,4-dihydro-4-isopropylidene-1-phenyl-5H-1,2-diazepin-5-one (**3c**): The black mixture was subjected to preparative TLC (2 mm silica gel, Merck, on glass plates, eluant ether/pentane 3:7). The yellow material, R_f = 0.22, was extracted with ethyl acetate. The solvent was evaporated to give yellow crystals which were recrystallized from *n*-pentane (–30°C). – IR (KBr): 1632 cm^{-1} (C=O). – UV ($CHCl_3$): λ_{max} (lg ε) = 317 (4.18), 343 nm (3.94). – ^1H NMR ($CDCl_3$): δ = 1.90 (s; 3H, *anti*-CH_3), 2.17 (s; 3H, *syn*-CH_3), 5.98 (s; 1H, 6-H), 7.45 (mc; 5H, C_6H_5), 7.61 (bs; 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 21.8 (q; *anti*-CH_3), 22.3 (q; *syn*-CH_3), 111.9 (d; C-6), 125.2 (d; C_6H_5, 2*o*-C), 127.4 (d; C_6H_5, *p*-C), 128.7 (d; C_6H_5, 2*m*-C), 131.0 (s; C-4), 144.0 (s; $C(CH_3)_2$), 146.1 (s; C_6H_5, *ipso*-C), 148.5 (d; C-3), 148.5 (s; C-7), 180.9 (s; C-5). – MS (70 eV): *m/z* = 260 (38%, M^+), 245 (1, M – CH_3), 225 (19, M – Cl), 169 (9, M – C_6H_5N), 77 (100, C_6H_5).

1,4-Dihydro-4-isopropylidene-1-methyl-5H-1,2-diazepin-5-one (**3d**) *and 1,5-Dihydro-5-isopropylidene-1-methyl-4H-1,2-diazepin-4-one* (**4d**): The brown mixture was evaporated to dryness and subjected to column chromatography (silica gel 60, 70–220 mesh, Macherey-Nagel). Dichloromethane elutes first orange colored **4d**, then (4 l CH_2Cl_2) most of the residual sydnone **1d**, and finally yellow **3d** was eluted by ethyl acetate, The fraction containing **4d** was evaporated in vacuo, digested with 20 ml of *n*-pentane, and kept at –78°C for

overnight. The yellow needles were collected at −10°C. The fraction containing **3d** was evaporated to a brownish oil which was extracted with *n*-pentane (7 × 50 ml). At −78°C **3d** crystallized as a yellow solid.

3d: IR (KBr): 1634 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 294 (3.96), 346 nm (3.63). – ^1H NMR ($CDCl_3$): δ = 1.91 (s; 3H, *anti*-CH_3), 2.04 (s; 3H, *syn*-CH_3), 3.57 (s; 3H, NCH_3), 5.41 (d, *J* = 9.8 Hz; 1H, 6-H), 6.78 (d, *J* = 9.8 Hz; 1H, 7-H), 7.27 (bs; 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 21.0 (q; *anti*-CH_3), 22.0 (q; *syn*-CH_3), 47.5 (q; NCH_3), 105.7 (d; C-6), 132.7 (s; C-4), 141.6 (d; C-3), 141.9 (s; $C(CH_3)_2$), 143.5 (d; C-7), 181.4 (s; C-5). – MS (70 eV): *m/z* = 164 (100%, M^+), 149 (21, M − CH_3), 135 (29, M − CH_3N).

4d: IR (Film): 1624 cm^{-1} (C=O). – UV ($CHCl_3$): λ_{max} (lg ε) = 272 (3.96), 295 (4.00), 414 nm (3.42). – ^1H NMR ($CDCl_3$): δ = 1.83 (s; 3H, *anti*-CH_3), 2.02 (s; 3H, *syn*-CH_3), 3.53 (s; 3H, NCH_3), 5.57 (bd, *J* = 9.8 Hz; 1H, 6-H), 6.16 (d, *J* = 9.8 Hz; 1H, 7-H), 6.98 (s; 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 21.6 (q; *anti*-CH_3), 22.2 (q; *syn*-CH_3), 47.8 (q; NCH_3), 109.1 (d; C-6), 130.1 (d; C-7), 131.2 (s; C-5), 134.8 (d; C-3), 137.5 (s; $C(CH_3)_2$), 179.5 (s; C-4). – MS (70 eV): *m/z* = 164 (56%, M^+), 149 (25, M − CH_3), 42 (100).

1-Benzyl-1,4-dihydro-4-isopropylidene-5H-1,2-diazepin-5-one (**3e**) *and 1-Benzyl-1,5-dihydro-5-isopropylidene-4H-1,2-diazepin-4-one* (**4e**): The mixture was evaporated and the oily residue was subjected to column chromatography (silica gel). Dichloromethane elutes **4e**, which was isolated by evaporation, dissolving in *n*-pentane, and storage of the pentane solution at −30°C for overnight. **4e** crystallizes in orange colored needles. Ethyl acetate elutes **3e** which was isolated as a yellow solid by the same procedure but keeping the pentane solution at −78°C.

3e: IR (KBr): 1635 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 294 (4.24), 345 nm (3.92). – ^1H NMR ($CDCl_3$): δ = 1.83 (s; 3H, *anti*-CH_3), 2.04 (s; 3H, *syn*-CH_3), 4.89 (s; 2H, CH_2), 5.45 (d, *J* = 9.7 Hz; 1H, 6-H), 6.90 (d, *J* = 9.7 Hz; 1H, 7-H), 7.24 (bs; 1H, 3-H), 7.38 (mc; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 20.9 (q; *anti*-CH_3), 22.0 (q; *syn*-CH_3), 63.5 (t; CH_2), 106.1 (d; C-6), 127.1 (d; C_6H_5, 2*o*-C), 127.8 (d; C_6H_5, *p*-C), 129.0 (d; C_6H_5, 2*m*-C), 132.8 (s; C-4), 136.4 (s; C_6H_5, *ipso*-C), 141.9 (s; $C(CH_3)_2$), 142.2 (d; C-3), 142.8 (d; C-7), 181.5 (s; C-5). – MS (70 eV): *m/z* = 240 (35%, M^+), 225 (1, M − CH_3), 135 (2, M − C_7H_7N), 91 (100, C_7H_7).

4e: IR (KBr): 1610 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 271 (3.96), 294 (3.98), 412 nm (3.21). – ^1H NMR ($CDCl_3$): δ = 1.80 (s; 3H, *anti*-CH_3), 2.00 (s; 3H, *syn*-CH_3), 4.83 (s; 2H, CH_2), 5.49 (bd, *J* = 10.0 Hz; 1H, 6-H), 6.17 (d, *J* = 10.0 Hz; 1H, 7-H), 7.01 (s; 1H, 3-H), 7.26 (mc; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 21.7 (q; *anti*-CH_3), 22.3 (q; *syn*-CH_3), 64.0 (t; CH_2), 109.1 (d; C-6), 127.3 (d; C_6H_5, 2*o*-C), 127.9 (d; C_6H_5, *p*-C), 128.6 (d; C_6H_5, 2*m*-C), 129.0 (d; C-7), 131.2 (s; C-5), 135.1 (d; C-3), 136.5 (s; C_6H_5, *ipso*-C), 137.6 (s; $C(CH_3)_2$), 179.9 (s; C-4). – MS (70 eV): *m/z* = 240 (35%, M^+), 135 (11, M − C_7H_7N), 91 (100, C_7H_7).

1,4-Dihydro-4-isopropylidene-1,7-dimethyl-5H-1,2-diazepin-5-one (**3f**): The mixture was evaporated and subjected to column chromatography (silica gel). Ethyl acetate elutes **3f**. Evaporation of the solvent yields a brown oil which crystallized. Recrystallization from ethyl acetate gave light yellow crystals at −30°C. – IR (KBr): 1654 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 303 (4.02), 346 nm (3.91). – ^1H NMR ($CDCl_3$): δ = 1.85 (s; 3H, *anti*-CH_3), 2.02 (s; 3H, *syn*-CH_3), 2.15 (s; 3H, 7-CH_3), 3.47 (s; 3H, NCH_3), 5.42 (s; 1H, 6-H), 7.19 (bs; 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (q; *anti*-CH_3), 21.7 (q; *syn*-CH_3), 24.3 (q; 7-CH_3), 68.2 (q; NCH_3), 107.9 (d; C-6), 131.3 (s; C-4), 141.9 (s; $C(CH_3)_2$), 143.9 (d; C-3), 153.1 (s; C-7), 181.1 (s; C-5). – MS (70 eV): *m/z* = 178 (75%, M^+), 163 (20, M − CH_3), 149 (29, M − CH_3N), 56 (100).

6,7,8,9-Tetrahydro-3-isopropylidenepyrido[1,2-b][1,2]diazepin-4(3H)-one (**3g**): The mixture was evaporated to a brown oil which was dissolved in 15 ml of ethyl acetate and kept at −78°C for overnight to give light yellow crystals. – IR (KBr): 1632 cm^{-1} (C=O). – UV ($CHCl_3$): λ_{max} (lg ε) = 269 (3.49), 306 (3.83), 348 nm (3.57). – ^1H NMR ($CDCl_3$): δ = 1.62–2.18 (m; 4H, CH_2CH_2-CH_2CH_2), 1.88 (s; 3H, *anti*-CH_3), 2.07 (s; 3H, *syn*-CH_3), 2.58 („t"; 2H, CH_2-6), 3.84 („t"; 2H, NCH_2), 5.43 (s; 1H, 5-H), 7.23 (bs, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 18.7, 22.1 (2 t; $CH_2CH_2CH_2CH_2$), 21.1 (q; *anti*-CH_3), 21.7 (q; *syn*-CH_3), 32.6 (t; CH_2-6), 53.6 (t; NCH_2), 106.1 (d; C-5), 131.8 (s; C-3), 141.4 (s; $C(CH_3)_2$), 143.5 (d; C-2), 154.0 (s; C-5a), 180.8 (s; C-4). – MS (70 eV): *m/z* = 204 (100%, M^+), 189 (20, M − CH_3).

7,8-Dihydro-3-isopropylidene-3H-pyrrolo[1,2-b][1,2]diazepin-4(6H)-one (**3h**): The mixture was evaporated and the residue subjected to column chromatography using silica gel. Ethyl acetate eluted **3h**. Evaporation to dryness and recrystallization from little ethyl acetate gave yellow needles. – IR (KBr): 1629 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 240 (3.98), 295 (4.02), 342 nm (3.69). – ^1H NMR ($CDCl_3$): δ = 1.85–2.30 (m; 2H, $CH_2CH_2CH_2$), 1.88 (s; 3H, *anti*-CH_3), 2.04 (s; 3H, *syn*-CH_3), 2.88 („t"; 2H, CH_2-6), 4.06 („t"; 2H, NCH_2), 5.50 (s; 1H, 5-H), 7.21 (bs; 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 19.9 (t; $CH_2CH_2CH_2$), 21.0 (q; *anti*-CH_3), 22.1 (q; *syn*-CH_3), 34.1 (t; CH_2-6), 58.0 (t; NCH_2), 102.3 (d; C-5), 132.4 (s; C-3), 141.8 (s; $C(CH_3)_2$), 142.3 (d; C-2), 156.2 (s; C-5a), 180.4 (s; C-4). – MS (70 eV): *m/z* = 190 (52%, M^+), 175 (9, M − CH_3), 42 (100).

1,4-Dihydro-4-[D_6]isopropylidene-1,7-dimethyl-5H-1,2-diazepin-5-one (**3i**): Analogous isolation as described for **3f** gave light yellow crystals. – ^1H NMR ($CDCl_3$): δ = 2.16 (s; 3H, 7-CH_3), 3.49 (s; 3H, NCH_3), 5.44 (s; 1H, 6-H), 7.23 (s; 1H, 3-H).

6,7,8,9-Tetrahydro-3-[D_6]isopropylidenepyrido[1,2-b][1,2]diazepin-4(3H)-one (**3j**): Analogous isolation as described for **3g** gave light yellow crystals. – ^1H NMR ($CDCl_3$): δ = 1.60–2.13 (m; 4H, $CH_2CH_2CH_2CH_2$), 2.56 („t"; 2H, CH_2-6), 3.79 („t"; 2H, NCH_2), 5.43 (s; 1H, 5-H), 7.23 (s; 1H, 2-H).

Table 7. Atomic parameters with standard deviations in parentheses. The equivalent isotropic thermal parameters (in 10^2 pm^2) of the C, N, and O atoms were calculated from the anisotropic U_{ij} by: $U_{eq} = (1/3)\,(U_{11}a^{*2}a^2 + \cdots + U_{23}b^*c^*bc \cdot \cos\alpha)$

Atom	x	y	z	U_{eq}, U_H
C(1)	0.5957(2)	0.3387(1)	0.6385(1)	2.14(4)
C(2)	0.4099(2)	0.2987(1)	0.5467(1)	2.04(4)
C(3)	0.3529(2)	0.1659(1)	0.5434(1)	2.05(4)
C(4)	0.4095(2)	0.1098(1)	0.6743(2)	2.57(5)
C(5)	0.5655(2)	0.1209(1)	0.7865(2)	2.45(5)
C(6)	0.2470(2)	0.1039(1)	0.4296(2)	2.36(5)
C(7)	0.1816(3)	0.1568(2)	0.2924(2)	3.31(6)
C(8)	0.1882(3)	-0.0290(2)	0.4321(2)	3.52(7)
C(9)	0.8830(2)	0.1660(2)	0.9330(2)	3.50(6)
N(1)	0.7174(2)	0.1915(1)	0.8110(1)	2.38(4)
N(2)	0.7275(2)	0.2926(1)	0.7454(1)	2.35(4)
O	0.3082(2)	0.3791(1)	0.4715(1)	2.95(4)
H(1)	0.631(3)	0.417(2)	0.610(2)	2.4(5)
H(4)	0.329(3)	0.055(2)	0.688(3)	4.2(6)
H(5)	0.587(3)	0.063(2)	0.869(2)	4.2(6)
H(71)	0.224(4)	0.243(2)	0.282(3)	5.8(8)
H(72)	0.048(3)	0.168(3)	0.246(3)	6.6(8)
H(73)	0.211(3)	0.103(2)	0.239(3)	5.0(7)
H(81)	0.192	-0.049	0.516	5.3
H(82)	0.264	-0.086	0.415	5.3
H(83)	0.067	-0.036	0.363	5.3
H(91)	0.896	0.236	0.990	5.3
H(92)	0.986	0.161	0.916	5.3
H(93)	0.874	0.090	0.975	5.3

Crystal Structure of **4d**[26]: A sample of the compound, which is a liquid at room temperature, was enclosed in a Lindemann capillary of 0.3 mm diameter. Crystal growth was performed on the diffractometer (Syntex $P2_1$ with a modified[29] low-temperature attachment LT-1). The sample was first quenched in the cold gas stream and the polycrystalline material obtained then transformed at 18°C into a single crystal by miniature zone-melting using focused heat radiation[30]. The crystallographic data and reflection intensities were measured at −130°C with graphite-monochromatized Mo-K_α radiation and a variable omega scan. Data of crystallography, diffractometry, and refinement are given in Table 4.

For the calculations the program system SHELXTL[31] was used on a Data General minicomputer Eclipse S/200. The structure was solved with direct methods. Only the ring H atoms could be located unambiguously in a difference Fourier map of the electron density, those of the methyl substituents were placed by structural modeling and only partly refined. Fig. 5 shows one molecule with its atomic thermal vibration ellipsoids[32] and torsional angles around the seven-membered ring system. The intermolecular packing is depicted in Fig. 6. The atomic parameters are listed in Table 7, the bond lengths and angles of the non-H atoms in Table 5[33].

CAS Registry Numbers

1a: 3483-16-7 / **1b**: 120-06-9 / **1c**: 5226-93-7 / **1d**: 6939-12-4 / **1e**: 16844-42-1 / **1f**: 4007-18-5 / **1g**: 105786-95-6 / **1h**: 86477-05-6 / **2a**: 39834-19-0 / **2b**: 105786-96-7 / **3a**: 105786-83-2 / **3b**: 105786-84-3 / **3c**: 105786-85-4 / **3d**: 105786-86-5 / **3e**: 105786-88-7 / **3f**: 105786-90-1 / **3g**: 105786-91-2 / **3h**: 105786-92-3 / **3i**: 105786-93-4 / **5j**: 105786-94-5 / **4d**: 105786-87-6 / **4e**: 105786-89-8

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[33] Further details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (West Germany). These data are available with quotation of the registry number CSD 51989, the authors, and the reference to this publication.

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