Bull Soc Chim Fr (1997) 134, 927-936

Antiaromatic compounds 30 [1]: The reactivity of a kinetically stabilized azete towards mesoionic compounds☆

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(Received 4 November 1997; accepted 15 December 1997)

Summary — The azete **1** reacts with the sydnones **7a–e** to furnish the 1*H*-triazepines **10a–e** after extrusion of CO_2. Photolysis of these compounds provides 2,2-dimethylpropanenitrile and the 1*H*-pyrazoles **14a–e** in quantitative yield. In the case of the reaction of **1** with the isomünchnone **15a** the primary product **16a** can be isolated by chromatography on silylated silica gel. Work-up of the reactions mixtures of **1** + **15a,b** on normal silica gel leads to the hydrolysis products **17a,b**. Both of these compounds are transformed to the 2*H*-pyrrole **18** by pyrolysis. Under thermal conditions, the münchnone **19** reacts as the open-chain ketene isomer **21** with the azete **1** by cycloaddition to give the oxaazabicyclo[2.2.0]hexene **20** as a mixture of *E*/*Z*-isomers. The 1,3-dithioliumolate **22** also avoids the direct cycloaddition with **1** and furnishes the bicyclic product **23** after cleavage of COS.

stable azete / mesoionic compound / cycloaddition / azaheterocycle / X-ray crystallography

Résumé — Composés antiaromatiques 30[1]: réactivité d'un azète cinétiquement stabilisé sur des composés mésoioniques. L'azète **1** réagit avec les sydnones **7a–e** pour fournir les 1*H*-triazépines **10a–e** avec extrusion de CO_2. La photolyse de ces composés fournit quantitativement du pivalonitrile et les 1*H*-pyrazoles **14a–e**. Dans le cas de la réaction de **1** et de l'isomünchnone **15a**, le produit primaire **16a** peut être isolé par chromatographie sur gel de silice. Le passage des mélanges réactionnels de **1** et **15a,b** sur du gel de silice normal conduit aux produits d'hydrolyse **17a,b**. Ces deux composés sont transformés par pyrolyse en 2*H*-pyrrole **18**. À chaud, la münchrome **19** réagit comme son isomère céténique à chaîne ouverte **21**. La cycloaddition de l'azète **1** et de **21** donne l'oxabicyclo[2.2.0]hexène **20** sous la forme d'un mélange d'isomères *E* et *Z*. Le 1,3-dithioliumolate **22** donne avec **1** le composé bicyclique **23** avec élimination de COS.

azète stable / composé mésoionique / cycloaddition / cristallographie aux rayons X

Introduction

Since the preparation of the first azete **1** that is stable and has the expected electronic structure at room temperature [2], its reactivity has been the subject of intensive investigations [3–5]. In spite of the presence of sterically demanding substituents, compound **1** participates in a surprisingly wide range of reactions (scheme 1).

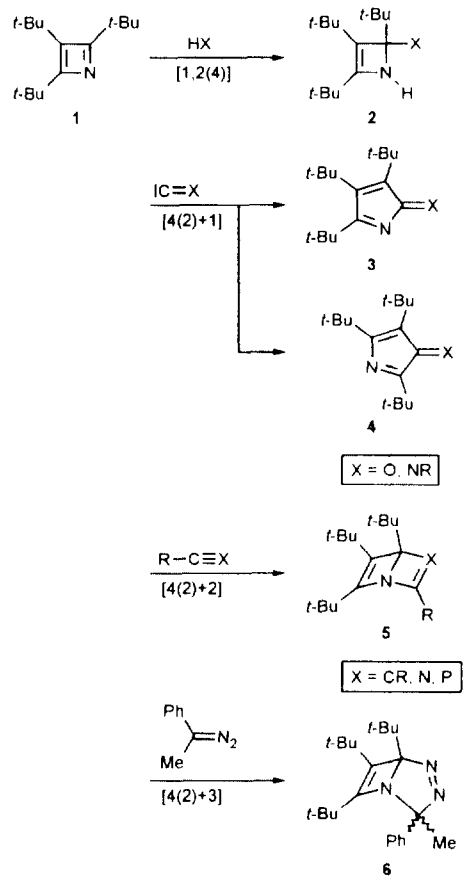
Thus, protic nucleophiles undergo [1,2(4)] additions with saturation of the C/N double bond to furnish the 1,2-dihydroazete (**1** → **2**) [6]. The cycloaddition potential of **1** is enormous. Carbon monoxide and isoelectronic isonitriles undergo addition at both double bonds in a [4(2) + 1] addition process [6]; the resultant bicyclic primary products, however, experience electrocyclic ring opening and the products isolated are the azacyclopentadiene derivatives **3** and **4**, respectively [6]. Electron-deficient acetylenes [7] as well as nitriles [8] and phosphaalkynes [5] undergo regiospecific addition with formation of the Dewar heteroaromatic compounds **5**; however, it is still not clear which of the cycloaddition types [4(2) + 1] is in operation. Only in the case of nitriles do the bicyclic products experience direct isomerization to the sterically highly encumbered pyrimidines. Finally, cycloadditions of diazo compounds to both the C/C and to the C/N double bonds of **1** (→ **6**) are known [5]. Comparable primary reactions have been observed with other 1,3-dipoles such as azides [10, 11] and nitrile oxides [12]. In the present work we compare the reactions of these acyclic dipoles with those of mesoionic compounds whose 1,3-dipolar nature is well known.

Reactions of 1 with sydnones 7a–e

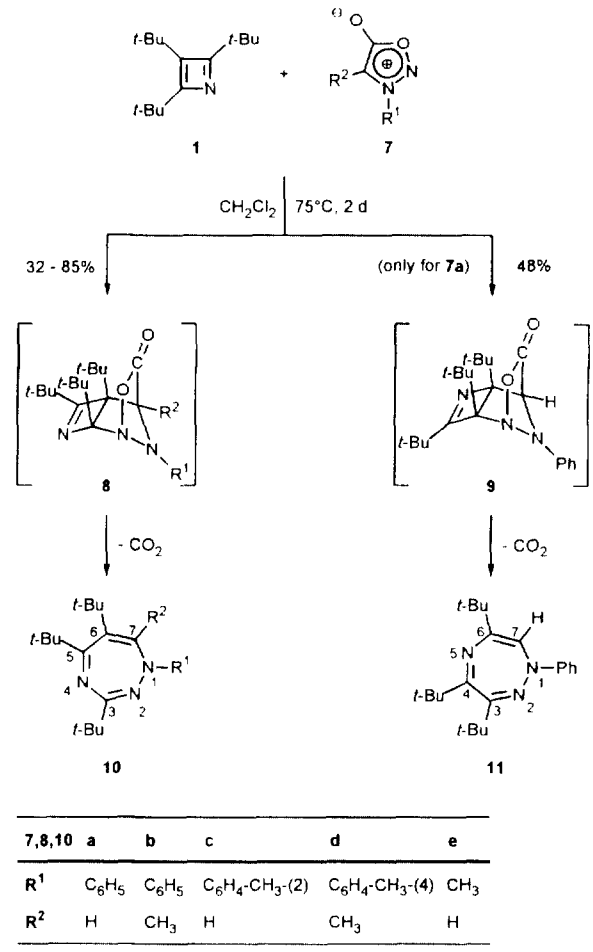
The 1*H*-triazepines **10a–e** and **11** are accessible from reactions of **1** with sydnones **7a–e**; thus, only in the case of **7a** is the cycloaddition not regiospecific (scheme 2).

☆ Dedicated to Professor CG Kreiter on the occasion of his 60th birthday.

* Correspondence and reprints



Scheme 1



Scheme 2

Formation of the triazepines is the result of an initial 1,3-dipolar cycloaddition of the azomethine imine dipole of **7** followed by extrusion of CO_2 from the primarily formed tricyclic species **8** and **9**, respectively. The latter product **11** was unambiguously characterized by elemental analysis and mass spectroscopic data. The formation of the 1*H*-1,2,5-triazepine **11**, isomeric to the 1*H*-1,2,4-triazepines **10a–e**, was only observed in the reaction with the sydnone **7a** and represents the major product of this process. It was not possible to influence the formation of isomers by variation of the substituents R^1 and R^2. The spectroscopic data for **10a–e** and **11** are in harmony with the proposed structures. The positions of the ^{13}C NMR signals for the skeletal carbon atoms C-3, C-5, C-6, and C-7 of **10a–e** unequivocally support the 1*H*-1,2,4-triazepine structure in which C-3 is linked to two nitrogen atoms and thus gives a signal at $\delta = 188.6 - 193.4$ with the largest shift to low field. The signals at $\delta = 167.8 - 172.0$ are due to the imine carbon atoms C-5. In all spectra, the signals of the carbon atom C-7 can be clearly identified by means of their splitting pattern. Thus, for **10a,c,e** it appears as a doublet with a characteristic $^1J_{C,H}$ coupling of 170 Hz in the sp^2-carbon region of the proton-coupled ^{13}C NMR spectra. In addition the constitutions were further supported by an X-ray crystallographic analysis of **10d** (fig 1).

The measured bond lengths and angles are in the expected ranges [13] and reflect the alternating double and single bonds in the triazepine ring which has a boat conformation. The double bond between C-6 and C-7 of 1.361(3) Å is the only one that is somewhat stretched. The reasons for this are the steric interactions between the substituent at C-6 and that at C-7. The methyl group at C-7 and the *t*-butyl group at C-6 are forced into a coplanar orientation by the sp^2 hybridization of the ring carbon atoms and so satisfy their spatial requirements by stretching the double bond.

The structure of **11**, the isomer of **10a**, is apparent from a comparison of its ^{13}C NMR data with those of 3,4,6-tri-*t*-butyl-1-trimethylsilyl-1*H*-1,2,5-triazepine (**11**, $SiMe_3$ in place of Ph), obtained from the reaction of **1** with diazo(trimethylsilyl)methane [10]. The structural difference between **10a** and **11** is most apparent from the chemical shifts of the C-7 signals, since that of **11** ($\delta = 117.8$) is 24.5 ppm toward higher field than the corresponding signal for **10a** ($\delta = 142.3$), which is attributable to the enamine character of the respective carbon atom. The above-mentioned results exclude the possibility of an initial cycloaddition at a C/N side of **1**.

Photolyses of the 1*H*-triazepines **10a–e** and **11** furnish the 1*H*-pyrazoles **14a–e** in yields of 85–93% (scheme 3); thermal transformations of this type have been reported [14, 15]. The course of the photochemical reaction can be followed by ^1H NMR spectroscopy on the basis of the low field shifts of the R^2 substituent signals. The cleavage of 2,2-dimethylpropanenitrile is

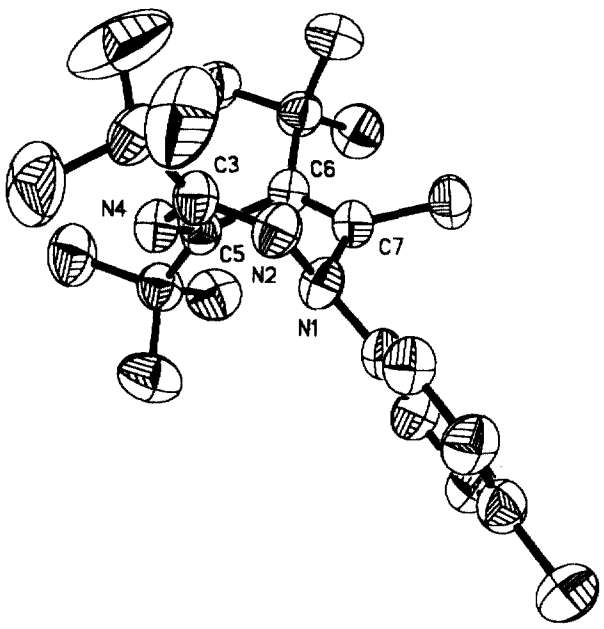


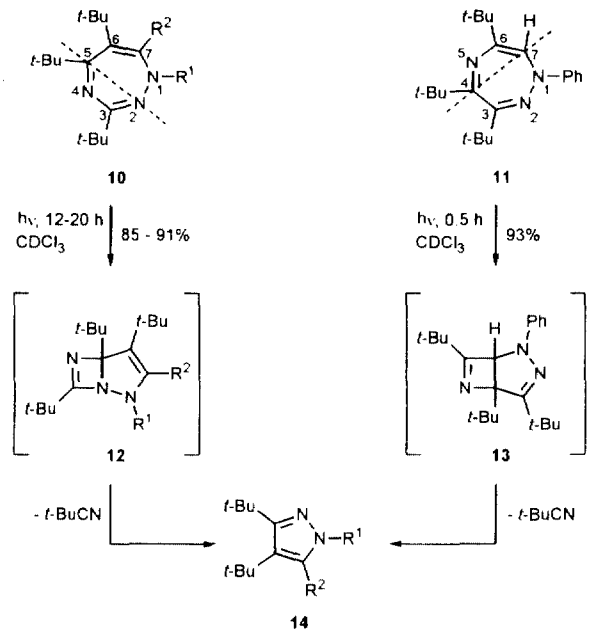
Fig 1. X-ray crystal structure of **10d** [34], selected bond lengths [pm] and bond angles [°]: N-1/N-2 143.7(2), N-2/C-3 130.0(3), C- 3/N-4 139.0(3), N-4/C-5 128.3(3), C-5/C-6 150.4(3), C-6/C-7 136.1(3), C-7/N-1 144.4(3); C-7/N-1/N-2 109.6(2), N-1/N-2/C-3 112.6(2), N-2/C-3/N-4 123.5(2), C-3/N-4/C-5 122.3, N-4/C-5/C-6 121.7(2), C-5/C-6/C-7 113.0(2), C-6/C-7/N-1 115.2(2).

confirmed by the appearance of the nitrile valency vibration in the IR spectra at $\nu = 2\,254$ cm^{-1}.

The results from the photolysis of **10a–e** and **11** indicate ring closures between N-2 and C-5 or C-4 and C-7, respectively. The thus formed bicyclic species **12** and **13** then eliminate 2,2-dimethylpropanenitrile to furnish the pyrazoles **14** which also provides indirect support for the constitutions of the starting 1*H*-triazepines. The transformations **10/11** → **14** are confirmed by the elemental analysis and mass spectroscopic data of the products. The ^{13}C NMR signals of the iminocarbon atoms of **14a–e** appear at rather low field ($\delta = 156.4$–158.4) which may be attributed to the *t*-butyl substituent on these carbon atoms. As expected, the carbon atoms C-4 and C-5 appear in the range $\delta = 125.1$–136.9. In spite of their very similar chemical shifts, the signals can easily be distinguished from each other and from the signals of the aromatic substituents R^1. In the cases of **14a,c,e**, identification of the C-5 signals is very easy on account of the large $^1J_{C,H}$ coupling constant of 183 Hz. In **14b,d**, C-5 can be identified on the basis of the $^2J_{C,H}$ coupling of 6 Hz with the protons of the methyl substituents.

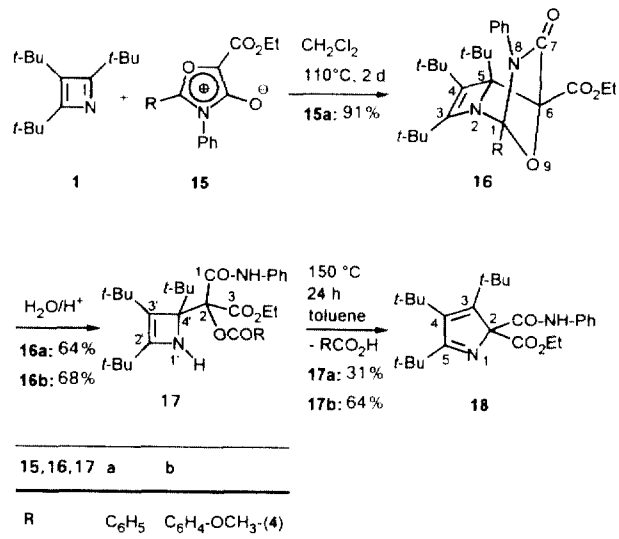
Reactions of 1 with isomünchnones 15a,b

Depending on the type of work-up of the crude mixture, the reaction of **1** with the isomünchnone **15a** furnishes either the primary, tricyclic adduct **16a** or its hydrolysis product **17a**. Analytically pure **16a** is obtained after separation at anhydrous silylated silica gel and **17a** with acidic silica gel; in the reaction of **1** + **15b** no attempt



10,12,14	a	b	c	d	e
R^1	C_6H_5	C_6H_5	C_6H_4-CH_3-(2)	C_6H_4-CH_3-(4)	CH_3
R^2	H	CH_3	H	CH_3	H

Scheme 3



15,16,17	a	b
R	C_6H_5	C_6H_4-OCH_3-(4)

Scheme 4

was made to isolate **16b** while **17b** was isolated and characterized (scheme 4).

The tricyclic compound **16** is the result of a regioselective [4(2) + 3] 1,3-dipolar cycloaddition of the carbonyl ylide dipole **15** to the azete **1**. The malonic monoamide **17** is formed by hydrolytic cleavage of the bonds C-1/N-2 and C-1/N-8 in **16**. The incorporation of water is immediately apparent from elemental analysis and mass spectroscopic data. The IR spectra reveal NH valency vibrations ($\nu = 3\,356$ and $3\,358$ cm^{-1}) as well as three carbonyl absorptions (see Experimental section). The hydrolysis sequence (**16** → **17**) is confirmed by an

X-ray crystallographic analysis of **17b** (fig 2). Within the limits of the standard deviations the dihydroazete ring in the molecule has an angular sum of 360° and is thus planar. The bond lengths and angles are as expected and require no further comment.

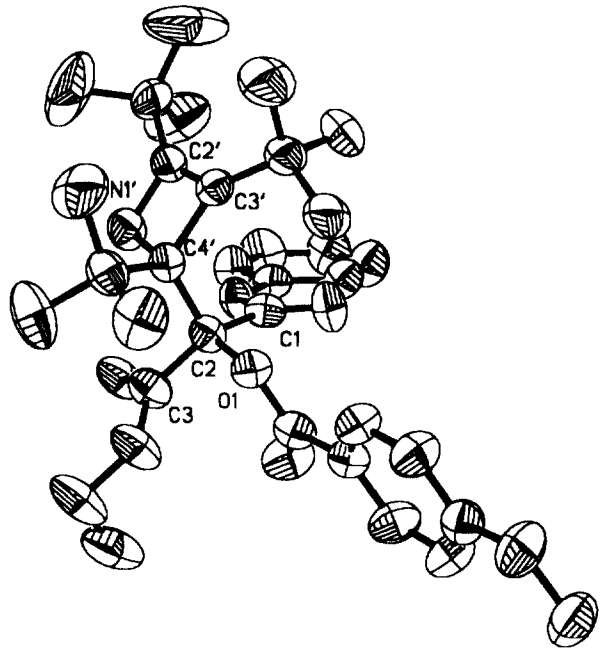


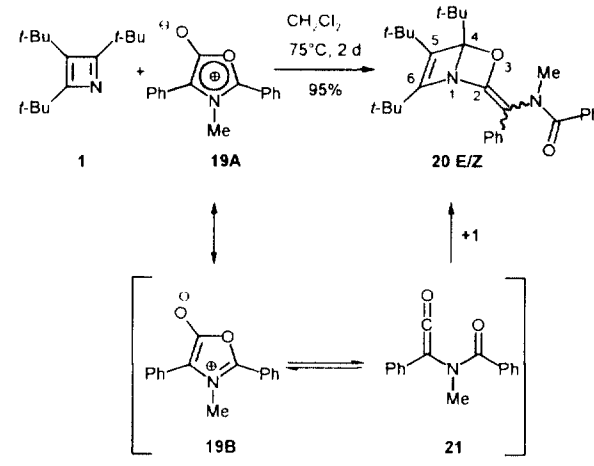
Fig 2. X-ray crystal structure of **17b** [34], selected bond lengths [pm] and bond angles [°]: C-2/O-1 143.0(4), C-2/C-1 158.4(5), C-2/C-3 154.4(5), C-2/C4′ 158.2(5), C-4′/N-1′ 150.5(5), N-1′/C-2′ 142.3(5), C-2′/C-3′ 134.7(6), C-3′/C-4′ 157.9(5); C-4′/C-2/C-1 110.2(3), C-4′/C-2/O-1 108.0(3), C-4′/C-2/C-3 110.4(3), C-3′/C-4′/C-2 115.9(3), C-3′/C-4′/N-1′ 84.7(3), N-1′/C-4′/C-2 106.3(3), C-4′/N-1′/C-2′ 88.9(3), N-1′/C-2′/C-3′ 97.2(4), C-2′/C-3′/C-4′ 88.7(3).

Confirmation of the structure of **17b** also confirms the regiochemistry of the preceding cycloaddition step. The constitution of the isolated primary adduct **16a** is reflected in its ^{13}C NMR spectrum: signals for three sp^3 [δ = 104.7 (C-1), 87.7 (C-5), 83.9 (C-6)] and for three sp^2 [δ = 169.7 (C-7), 158.8 (C-3), 144.4 (C-4)] carbon atoms are present.

Thermolyses of **17a** and **b** in toluene at 150 °C in Schlenk pressure tubes furnished in both cases the same 2*H*-pyrazole **18** after chromatographic work-up. The cleavage of benzoic or, respectively, 4-methoxybenzoic acid is obvious from the absence of signals in the methoxy and aromatic regions as well as the disappearance of the NH signal (δ = 10.1) in the ^1H NMR spectrum of **18**. Elemental analysis and molecular mass (MS) determinations further support the given transformation. The question of whether an azahausene is formed as an intermediate in the thermolysis reaction remains unanswered. In the ^{13}C NMR spectrum of **18** the signal for C-2 appears at δ = 78.2, carbon atoms C-3 (162.1), C-4 (150.1), and C-5 (183.3) give rise to signals at considerably lower field. The signal for the iminocarbon atom C-5 is broadened (small $^3J_{C,H}$ coupling) and thus easily discernible from those of the carbonyl carbon atoms.

Reactions of 1 with münchnone 19

Münchnones usually react with multiple bond systems as azomethine ylides by a [3 + 2] cycloaddition process [16, 17]. Under thermal conditions, however, they exist in equilibrium with their open-chain ketene forms [18, 19] and can react as such. This also holds for the reaction of azete **1** with **19** at 75 °C leading to an isomeric mixture of *E*/*Z*-**20** which can be purified by column chromatography but not separated. Thus, formation of the bicyclic species at the sterically better accessible C/N edge of **1** must be preceded by the electrocyclic ring opening of the münchnone (**19A** ↔ **19B** → **21**). Evidence for the development of the dipole reactivity of **19** (NMR examination of the crude product solution) which would then lead to the formation of diazepines (cf, reaction **1** + **7** → **10**, **11**) could not be found (scheme 5).



Scheme 5

Elemental composition and molecular mass determinations at first confirmed the 1:1 reaction without elimination of CO_2. The close relationship of the two stereoisomers (*E*- and *Z*-**20**) can be recognized from the double, closely spaced signal sets in the ^1H and ^{13}C NMR spectra; integration of the *N*-methyl signals demonstrates a ratio of 60:40 but without allowing assignments to *E*- and *Z*-isomers (see Experimental section).

As an example for the structure elucidation, a brief discussion of the ^{13}C NMR data for the 'minor' product is given. The rather broad singlets for the olefinic carbon atoms C-5 and C-6 (δ = 140.8 and 164.8, respectively), as also revealed by the proton-coupled ^{13}C NMR spectrum, show that the cycloaddition of the benzoylaminoketene has occurred at neighboring carbon and nitrogen atoms (see also discussion on the structure of **18**); the signal for C-4 (δ = 110.0) exhibits the same phenomenon. Consequently, it is lacking in the signal for the exocyclic benzylidene carbon atom (δ = 108.0); the two donor substituents on the bicyclic system are responsible for the relatively high field position of this signal. As expected the signal for C-2 (δ = 158.6) appears at appreciably lower field. The signal for the amide carbonyl carbon atom experiences

the highest deshielding (δ = 173.1), the absence of further carbonyl carbon atoms is in full accord with the reaction of the ketene function of **21** with **1**. It should be mentioned here that the reaction of diphenylketene with the azete **1** is known to proceed by [4(2) + 2] cycloaddition at the carbonyl group [20].

Final confirmation of the structure of the two geometrical isomers of **20** was provided by X-ray crystallography. Crystallization of the analytically pure mixture from *n*-pentane (slow evaporation of the solvent over a rubber stopper at 25 °C) furnished a suitable single crystal. This proved to be *Z*-**20** but a correlation with the NMR data (major or minor product) was not possible (fig 3).

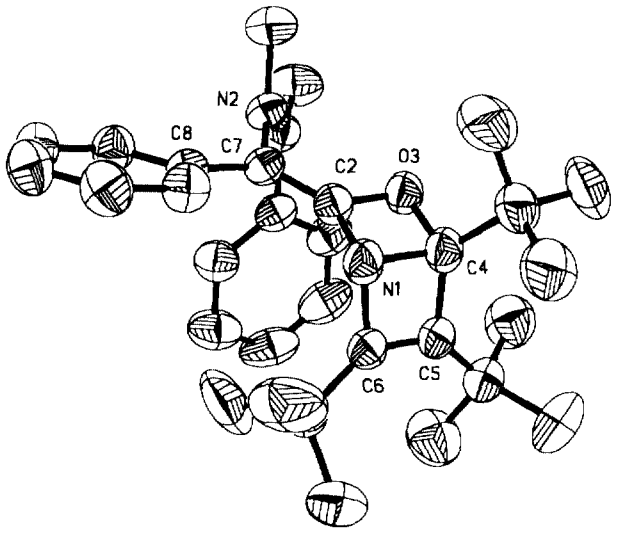
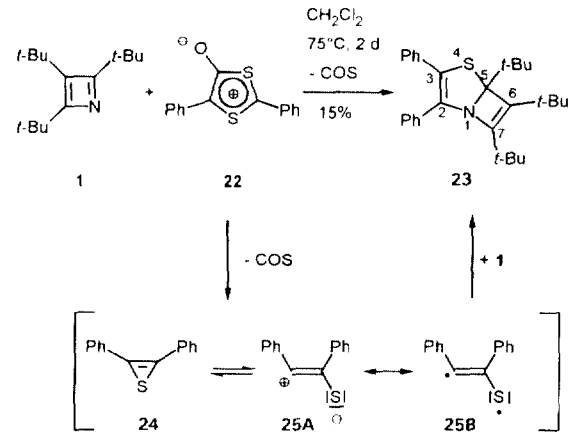


Fig 3. X-ray crystal structure of *Z*-**20** [34], selected bond lengths [pm] and bond angles [°]: N-1/C-2 144.1(3), C-2/C-7 132.2(3), C-7/C-8 149.8(3), C-7/N-2 144.2(3), C-2/O-3 139.3(3), O-3/C-4 146.9(3), C-4/N-1 153.1(3), C-4/C-5 152.6(4), C-5/C-6 136.5(4), C-6/N-1 149.8(3), N-1/C-2/O-3 98.7(2), N-1/C-2/C-7 134.9(2), O-3/C-2/C-7 126.2(2), C-2/C-7/C-8 125.3(2), C-2/C-7/N-2 115.8(2), N-2/C-7/C-8 118.4(2),C-2/O-3/C-4 86.9(2), O-3/C-4/N-1 91.5(2), O-3/C-4/C-5 113.9(2), N-1/C-4/C-5 88.4(2), C-4/C-5/C-6 90.2(2), C-5/C-6/N-1 96.1(2), C-6/N-1/C-4 85.2(2), C-6/N-1/C-2 114.3(2), C-2/N-1/C-4 82.9(2).

The bond lengths of the bicyclic compound *Z*-**20** reflect the ring strain in the molecule. The zero bridging bond N-1/C-4 length of 1.531(3) Å is stretched (average bond length: 1.469 Å) [13]. Also the C-5/C-6 double bond bearing bulky *t*-butyl groups is stretched to 1.365(4) Å (average bond length: 1.316 Å) [13]. The folding angle between the two least-squares planes N-1/C-4/O-3/C-2 and N-1/C-4/C-5/C-6 amounts to 114.6°.

Reactions of 1 with the 1,3-dithiolium-4-olate 22

Finally, the reactivity of the cyclic thiocarbonyl ylide **22** towards azete **1** was examined. This unexpected reaction, performed in dichloromethane at 75 °C, proceeded through elimination of COS to furnish the 1-aza-4-thiabicyclo[3.2.0]hepta-2,6-diene **23** in modest (15%) yield. It can be rationalized in terms of a [3 + 2] cycloaddition of the sextet dipole **25A** ↔ **25B** at the C/N edge of **1** (scheme 6).



Scheme 6

As in the previously mentioned case, product formation is not preceded by a [4(2) + 3] cycloaddition of the mesoionic species **22**; instead, the product is only compatible with initial elimination of COS, and formation of the intermediate **25A** ↔ **25B** which, in turn, demands that the thiirene **24** be an intermediate in this reaction path. Whether intermediate **24** undergoes ionic (→ **25A**) or radical (→ **25B**) ring opening cannot be decided [21–24].

The constitution of the bicyclic product **23** cannot be unambiguously deduced from its spectroscopic data (see Experimental section). Elemental analysis and mass spectroscopy (m/z = 431, M^+) merely reveal that the product has been formed under elimination of COS. Final structural elucidation required X-ray crystallographic analysis of a suitable crystal of **23** (from chloroform) (fig 4).

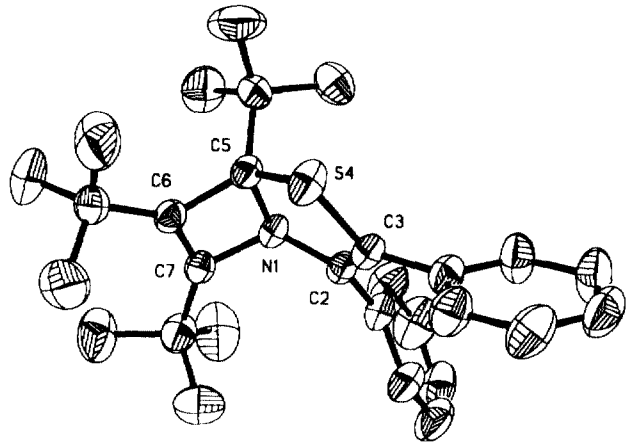


Fig 4. X-ray crystal structure of **23** [34], selected bond lengths [pm] and bond angles [°]: S-4/C-3 176.9(4), C-3/C-2 131.7(5), C-2/N-1 145.4(4), N-1/C-5 151.6(4), N-1/C-7 148.3(4), C-7/C-6 134.2(5), C-6/C-5 153.4(5), C-5/S-4 184.7(4), S-4/C-3/C-2 114.3(3), C-3/C-2/N-1 116.4(3), C-2/N-1/C-5 110.4(3), C-2/N-1/C-7 119.8(3), C-5/N-1/C-7 86.8(2), N-1/C-7/C-6 95.5(3), C-7/C-6/C-5 91.1(3), C-6/C-5/N-1 86.7(3), C-6/C-5/S-4 112.8(2), N-1/C-5/S-4 107.0(2), C-5/S-4/C-3 91.1(2).

This demonstrates the seven-membered bicyclic ring structure with a folding angle of 119.1° between the least-squares planes N-1/C-2/C-3/S-4/C-5 and N-1/C-7/C-6/C-5 and the two almost planar rings. The bond lengths in the bicyclic structure are in the expected ranges and require no further comment with the exception of the zero bridging bond N-1/C-5 which is somewhat stretched to 1.516(4) Å on account of the ring strain.

Experimental section

All reactions were carried out under argon (purity >99.008%) in a previously baked out and evacuated apparatus (standard Schlenk techniques). Solvents were dried by standard methods (diethyl ether, *n*-pentane: Na/K alloy; CH_2Cl_2: P_4O_{10}), then distilled, and stored under argon. Melting points are uncorrected. Microanalyses: Perkin-Elmer Analyser 240. FT-IR: Perkin-Elmer 16 PC. MS: Finnigan MAT 90. ^1H NMR and ^{13}C NMR: Bruker AMX 400 at 400 MHz (^1H) and 101 MHz (^{13}C). Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) for ^1H or the solvent (^{13}C) as internal standards. Coupling constants (J) are reported in Hertz (Hz) and are only given for ^{13}C when they reveal some important structural information.

Column chromatography was formed in water-cooled glass tubes with a positive pressure of argon on the column. The eluate was monitored by TLC. Silica gel and neutral aluminum oxide were heated for 3 h under vacuum and then deactivated with 4% water. Silylated silica gel was used for the separation of **16a**.

Compounds **7a** [25], **7b** [26], **7c** [27], **7d** and **7e** [28], **15a** [30], **15b** [29], and **22** [31] were prepared according to the reported procedures.

Caution: When reactions are performed in Schlenk pressure tubes at elevated temperatures, additional safety shields should be used.

Synthesis of 1H-triazepines **10a–e, 11**: *general procedure*

A solution of equimolar amounts of azete **1** and sydnone **7** in CH_2Cl_2 (20 mL) was heated for 48 h at 75 °C with magnetic stirring in a Schlenk pressure tube. After evaporation of the solvent under vacuum (20 °C/0.001 mbar) crude products **10** and **11** were obtained as yellow oils. Purification by column chromatography on silica gel with *n*-pentane/diethyl ether mixtures as eluent (after starting with *n*-pentane, Et_2O was successively added in 1 mL portions until the yellow product began to move) gave **10a,c,e** as yellow oils and **10b,d** as yellow solids.

- *3,5,6-Tri-tert-butyl-1-phenyl-1H-1,2,4-triazepine* **10a** *and 3,4,6-tri-tert-butyl-1-phenyl-1H-1,2,5-triazepine* **11**

From **1** (0.44 g, 2.0 mmol) and **7a** (0.32 g, 2.0 mmol) to afford 0.32 g (48%) of **11** (the first yellow fraction eluted from the column) as a yellow oil.

IR (CH_2Cl_2): ν = 2 966, 2 929, 2 870, 1 599, 1 501, 1 491, 1 458 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.20, 1.22, 1.29 (each s, each 9H, *t*Bu), 5.69 (s, 1H, H-7), 6.91 (t, 1H, $^3J_{H,H}$ = 7.4, H-phenyl), 6.99 (d, 2H, $^3J_{H,H}$ = 8.7, H-phenyl), 7.24 (d, 2H, $^3J_{H,H}$ = 7.4, H-phenyl).

^{13}C NMR ($CDCl_3$): δ = 29.3, 29.7, 31.1 [C(CH_3)$_3$], 34.3, 36.5, 39.7 [C(CH_3)$_3$], 113.8 (*ortho*-C), 117.8 (d, $^1J_{C,H}$ = 171, C-7), 120.8 (*para*-C), 128.6 (*meta*-C), 148.7 (*ipso*-C), 155.4 (C-6), 172.1 (C-4), 185.3 (C- 3).

MS (EI, 70 eV): *m/z* (%) = 339 (18, M^+), 324 (16, M^+ – CH_3), 256 (8, M^+ – C_4H_9CN), 241 (100), 57 (38, $C_4H_9^+$).

Anal calc for $C_{22}H_{33}N_3$, 339.50: C, 77.83; H, 9.80; N, 12.37. Found: C, 78.1; H, 9.9; N, 11.4.

Further elution of the second yellow fraction in the column gave 0.22 g (32%) of **10a** as a yellow oil.

IR (CH_2Cl_2): ν = 2 967, 2 929, 2 871, 1 721, 1 623, 1 596, 1 458 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.24 (s, 9H, *t*Bu), 1.27 (s, 18H, *t*Bu), 6.28 (s, 1H, H-7), 6.88 (t, 1H, $^3J_{H,H}$ = 7.4, H-phenyl), 7.07 (d, 2H, $^3J_{H,H}$ = 8.7, H-phenyl), 7.23 (d, 2H, $^3J_{H,H}$ = 7.4, H-phenyl).

^{13}C NMR ($CDCl_3$): δ = 28.6, 29.9, 32.5 [C(CH_3)$_3$], 33.5, 36.6, 41.2 [C(CH_3)$_3$], 113.7 (*ortho*-C), 120.6 (*para*-C), 128.6 (*meta*-C), 141.6 (C-6), 142.3 (d, $^1J_{C,H}$ = 171, C-7), 149.0 (*ipso*-C), 170.5 (C-5), 189.2 (C-3).

MS (EI, 70 eV): *m/z* (%) = 339 (81, M^+), 324 (99, M^+ – CH_3), 256 (8, M^+ – C_4H_9CN), 241 (100), 57 (3, $C_4H_9^+$).

- *3,5,6-Tri-tert-butyl-7-methyl-1-phenyl-1H-1,2,4-triazepine* **10b**

From **1** (0.44 g, 2.0 mmol) and **7b** (0.35 g, 2.0 mmol) to afford 0.59 g (83%) of **10b** as a yellow oil, recrystallization from *n*-pentane furnished yellow crystals. Mp 54 °C.

IR (CCl_4): ν = 2 966, 2 868, 1 619, 1 583, 1 485, 1 458 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.20, 1.24, 1.28 (each s, each 9H, *t*Bu), 1.92 (s, 3H, 7-CH_3), 6.80 (t, 1H, $^3J_{H,H}$ = 7.2, H-phenyl), 7.02 (d, 2H, $^3J_{H,H}$ = 8.4, H-phenyl), 7.19 (d, 2H, $^3J_{H,H}$ = 7.2, H-phenyl).

^{13}C NMR ($CDCl_3$): δ = 14.8 (q, $^1J_{C,H}$ = 136, 7-CH_3), 28.6, 30.1, 30.6 [C(CH_3)$_3$], 32.7, 36.3, 41.0 [C(CH_3)$_3$], 114.7 (*ortho*-C), 119.4 (*para*-C), 128.5 (*meta*-C), 138.7 (C-6), 145.8 (*ipso*-C), 147.9 (q, $^2J_{C,H}$ = 7, C-7), 172.0 (C-5), 193.3 (C-3).

MS (EI, 70 eV): *m/z* (%) = 353 (35, M^+), 338 (100, M^+ – CH_3), 296 (10, M^+ – C_4H_9CN), 255 (51, M^+ – $C_5H_{10}N_2$), 118 (98, M^+ – CH_3CNPh), 77 (39, Ph^+), 57 (38, $C_4H_9^+$).

Anal calc for $C_{23}H_{35}N_3$, 353.53: C, 78.14; H, 9.98; N, 11.89. Found: C, 78.2; H, 9.9; N, 11.6.

- *3,5,6-Tri-tert-butyl-1-o-tolyl-1H-1,2,4-triazepine* **10c**

From **1** (0.44 g, 2.0 mmol) and **7c** (0.35 g, 2.0 mmol) to afford 0.30 g (42%) of **10b** as a yellow oil.

IR (CCl_4): ν = 2 966, 2 868, 1 619, 1 583, 1 484, 1 462, 1 364 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.12, 1.17, 1.27 (each s, each 9H, *t*Bu), 2.16 (s, 3H, *ortho*-CH_3), 5.96 (s, 1H, CH), 6.86 (t, 1H, $^3J_{H,H}$ = 7.4, H-phenyl), 7.02 (d, 1H, $^3J_{H,H}$ = 6.9, H-phenyl), 7.10 (d, 2H, $^3J_{H,H}$ = 8.8, H-phenyl), 7.78 (d, 1H, $^3J_{H,H}$ = 8.4, H-phenyl).

^{13}C NMR ($CDCl_3$): δ = 19.9 (*ortho*-CH_3), 28.4, 30.2, 32.7 [C(CH_3)$_3$], 33.3, 36.6, 40.9 [C(CH_3)$_3$], 118.2, 122.7, 126.4 (C-arom), 128.0 (*ortho*-C), 131.1 (C-arom), 138.4 (C-6), 146.9 (q, $^1J_{C,H}$ = 170, C-7), 148.9 (*ipso*-C), 168.1 (C-5), 188.4 (C-3).

MS (EI, 70 eV): *m/z* (%) = 353 (52, M^+), 338 (89, M^+ – CH_3), 296 (19, M^+ – C_4H_9CN), 255 (92, M^+ – $C_5H_{10}N_2$), 91 (46, $PhCH_3^+$), 57 (100, $C_4H_9^+$).

- *3,5,6-Tri-tert-butyl-7-methyl-1-p-tolyl-1H-1,2,4-triazepine* **10d**

From **1** (0.44 g, 2.0 mmol) and **7d** (0.38 g, 2.0 mmol) to afford 0.54 g (73%) of **10d** as a yellow oil, recrystallization from *n*-pentane furnished yellow crystals. Mp 90 °C.

IR (CCl_4): ν = 2967, 2925, 2869, 1613, 1583, 1508, 1478 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.12, 1.14, 1.18 (each s, each 9H, *t*Bu), 1.80 (s, 3H, *para*-CH_3), 2.16 (s, 3H, C-CH_3), 6.87 (d, 2H, $^3J_{H,H}$ = 8.5, H-arom), 6.92 (d, 2H, $^3J_{H,H}$ = 7.9, H-arom).

^{13}C NMR ($CDCl_3$): δ = 14.8 (7-CH_3), 20.6 (*para*-CH_3), 28.6, 30.2, 30.7 [C(CH_3)$_3$], 32.7, 36.3, 41.0 [C(CH_3)$_3$], 115.0 (*ortho*-C), 128.6 (*para*-C), 129.1 (*meta*-C), 138.2 (C-6), 143.7 (*ipso*-C), 148.4 (C-7), 171.6 (C-5), 193.4 (C-3).

MS (EI, 70 eV): *m/z* (%) = 367 (34, M^+), 352 (100, M^+ – CH_3), 269 (42, M^+ – C_4H_9), 132 (99, M^+ – $C_5H_{10}N_2$), 91 (40, $PhCH_3^+$), 57 (81, $C_4H_9^+$).

Anal calc for $C_{24}H_{37}N_3$, 367.58: C, 78.42; H, 10.15; N, 11.43. Found: C, 78.1; H, 10.3; N, 10.9.

• *3,5,6-Tri-tert-butyl-1-methyl-1H-1,2,4-triazepine* **10e**

From **1** (0.44 g, 2.0 mmol) and **73** (0.20 g, 2.0 mmol) to afford 0.47 g (85%) of **10e** as a yellow oil.

IR (CH_2Cl_2): ν = 2966, 2868, 1621, 1583, 1479 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.07, 1.09, 1.20 (each s, each 9H, *t*Bu), 2.56 (s, 3H, N–CH_3), 5.82 (s, 1H, H-7).

^{13}C NMR ($CDCl_3$): δ = 28.5, 30.1, 32.6 [C(CH_3)$_3$], 33.1, 35.9, 40.9 [C(CH_3)$_3$], 44.6 (td, $^1J_{C,H}$ = 166, $^3J_{C,H}$ = 6, N–CH_3), 167.8 (C-5), 166.6 (C-3).

MS (EI, 70 eV): *m/z* (%) = 277 (27, M^+), 262 (100, M^+ – $C_5H_{10}N_2$), 179 (38, M^+ – $C_4H_9^+$), 57 (93, $C_4H_9^+$).

Synthesis of 1H-pyrazoles **14a–e**: *general procedure*

A solution of the 1*H*-triazepine **10a–e** or **11** in CD_2Cl_2 (2 mL) was irradiated with a high-pressure mercury lamp ($\lambda \leqslant 280$ nm) and the reaction was monitored by ^1H NMR spectroscopy. After evaporation of the solvent under vacuum (20 °C/0.001 mbar) crude products **14** were obtained as yellow oils. Purification by column chromatography on silica gel or neutral aluminum oxide with *n*-pentane/diethyl ether (10:1) as eluent gave products **14a–e** as colorless solids.

• *3,4-Di-tert-butyl-1-phenyl-1H-pyrazole* **14a**

From **10a** or **11** (0.2 g, 0.78 mmol) to afford 0.17 g (85%) (from **10a**; irradiation time: 12 h) or 0.19 g (93%) (from **11**; irradiation time: 0.5 h) of **14a** as a colorless solid after purification on silica gel.

IR (CCl_4): ν = 2960, 2929, 2360, 1730, 1602, 1500 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.41, 1.50 (each s, each 9H, *t*Bu), 7.13 (t, 1H, $^3J_{H,H}$ = 7.3, H-phenyl), 7.34 (t, 2H, $^3J_{H,H}$ = 7.3, H-phenyl), 7.64 (d, 2H, $^3J_{H,H}$ = 8.5, H-phenyl), 7.68 (s, 1H, H-5).

^{13}C NMR ($CDCl_3$): δ = 30.8 [C(CH_3)$_3$], 31.7, 32.9 [C(CH_3)$_3$], 34.2 [C(CH_3)$_3$], 117.9 (*ortho*-C), 125.1 (*para*-C), 125.3 (d, $^1J_{C,H}$ = 183, C-5), 129.1 (*meta*-C), 130.8 (C-4), 140.1 (*ipso*-C), 158.4 (C-3).

MS (EI, 70 eV): *m/z* (%) = 256 (20, M^+), 257 (4, M^+ + H), 241 (100, M^+ – CH_3), 199 (9, M^+ – C_4H_9), 57 (12, $C_4H_9^+$).

Anal calc for $C_{17}H_{24}N_2$, 256.39: C, 79.64; H, 9.44; N, 10.93. Found: C, 78.5; H, 9.5; N, 10.0.

• *3,4-Di-tert-butyl-5-methyl-1-phenyl-1H-pyrazole* **14b**

From **10b** (0.2 g, 0.57 mmol) to afford (irradiation time: 14 h) 0.14 g (91%) of **14b** as a colorless solid after purification on neutral aluminum oxide.

IR (CCl_4): ν = 2958, 2924, 1598, 1500 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.41 (s, 18H, *t*Bu), 2.25 (s, 3H, 5-CH_3), 7.30 (s, 5H, H-phenyl).

^{13}C NMR ($CDCl_3$): δ = 17.7 (5-CH_3), 31.6 [C(CH_3)$_3$], 32.2, 33.4 [C(CH_3)$_3$], 34.2 [C(CH_3)$_3$], 125.3, 125.8 (arom-C), 127.0 (C-4), 128.7 (*para*-C), 135.4 (q, $^2J_{C,H}$ = 6, C-5), 140.1 (*ipso*-C), 157.0 (C-3).

MS (EI, 70 eV): *m/z* (%) = 270 (17, M^+), 255 (100, M^+ – CH_3), 77 (17, Ph^+), 57 (10, $C_4H_9^+$).

Anal calc for $C_{18}H_{26}N_2$, 270.42: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.9; H, 9.7; N, 10.3.

• *3,4-Di-tert-butyl-1-o-tolyl-1H-pyrazole* **14c**

From **10c** (0.2 g, 0.57 mmol) to afford (irradiation time: 20 h) 0.14 g (91%) of **14c** as a colorless solid after purification on silica gel.

IR (CCl_4): ν = 2958, 2917, 2870, 1535, 1500, 1483, 1462 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.34, 1.40 (each s, each 9H, *t*Bu), 2.23 (s, 3H, *ortho*-CH_3), 7.1–7.19 (m, 3H, H-arom), 7.23–7.26 (m, 1H, H-arom), 7.31 (s, H-5).

^{13}C NMR ($CDCl_3$): δ = 18.7 (*ortho*-CH_3), 30.7 [C(CH_3)$_3$], 31.9, 33.0 [C(CH_3)$_3$], 33.9 [C(CH_3)$_3$], 125.1, 126.4, 127.2 (arom-C), 129.1 (*ortho*-C-CH_3), 129.4 (d, $^1J_{C,H}$ = 183, C-5), 131.5 (arom-C), 133.1 (C-4), 140.1 (*ipso*-C), 157.5 (C-3).

MS (EI, 70 eV): *m/z* (%) = 270 (27, M^+), 255 (100, M^+ – CH_3), 77 (14, Ph^+), 57 (10, $C_4H_9^+$).

• *3,4-Di-tert-butyl-5-methyl-1-p-tolyl-1H-pyrazole* **14d**

From **10d** (0.2 g, 0.54 mmol) to afford (irradiation time: 14 h) 0.14 g (91%) of **14d** as a colorless solid after purification on neutral aluminum oxide.

IR (CCl_4): ν = 2958, 2869, 1723, 1613, 1521, 1478, 1430 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.40 (s, 18H, *t*Bu), 2.24 (s, 3H, 5-CH_3), 2.30 (s, 3H, *para*-CH_3), 7.15 (d, 2H, $^3J_{H,H}$ = 8.6, H-arom), 7.19 (d, 2H, $^3J_{H,H}$ = 8.6, H-arom).

^{13}C NMR ($CDCl_3$): δ = 15.7 (C-5-CH_3), 21.0 (*para*-CH_3), 31.6 [C(CH_3)$_3$], 32.3, 33.5 [C(CH_3)$_3$], 34.2 [C(CH_3)$_3$], 125.1 (C-4), 125.8 (*ortho*-CH_3), 129.3 (*meta*-C), 135.5 (*para*-C), 136.9 (q, $^2J_{C,H}$ = 6, C-5), 137.8 (*ipso*-C), 156.8 (C-3).

MS (EI, 70 eV): *m/z* (%) = 284 (15, M^+), 269 (100, M^+ – CH_3), 91 (14, $C_7H_7^+$), 57 (4, $C_4H_9^+$).

• *3,4-Di-tert-butyl-1-methyl-1H-pyrazole* **14e**

From **10e** (0.2 g, 0.72 mmol) to afford (irradiation time: 14 h) 0.12 g (85%) of **14e** as a colorless solid after purification on silica gel.

IR (CCl_4): ν = 2967, 2872, 1671, 1478, 1460, 1365 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.37, 1.42 (each s, each 9H, *t*Bu), 3.37 (s, 3H, N–CH_3), 7.13 (s, 1H, H-5).

^{13}C NMR ($CDCl_3$): δ = 30.6 [C(CH_3)$_3$], 31.9, 33.0 [C(CH_3)$_3$], 33.6 [C(CH_3)$_3$], 38.3 (N–CH_3), 128.2 (C-4), 129.7 (d, $^1J_{C,H}$ = 182, C-5), 156.4 (C-3).

MS (EI, 70 eV): *m/z* (%) = 194 (16, M^+), 179 (100, M^+ – CH_3), 57 (14, $C_4H_9^+$).

Synthesis of ethyl 1,8-diphenyl-7-oxo-3,4,5-tri-tert-butyl-2,8-diaza-9-oxatricyclo[4.2.1.0^{2,5}]non-3-ene-6-carboxylate **16a**

A solution of **1** (0.55 g, 2.5 mmol) and **15a** (0.80 g, 2.6 mmol) in CH_2Cl_2 (20 mL) was heated for 48 h at 110 °C with magnetic stirring in a Schlenk pressure tube. After evaporation of the solvent under vacuum (20 °C/0.001 mbar) the

product was obtained as a yellow oil. Purification by column chromatography on silylated silica gel using *n*-pentane as eluent furnished 1.22 g (91%) of **16a** as a colorless oil.

IR (CCl_4): ν = 2 965, 2 930, 1 769 (C=O), 1 743 (C=O), 1 499, 1 478, 1 450, 1 382, 1 363 cm^{-1}.

^1H NMR (CD_2Cl_2): δ = 0.97 (s, 9H, *t*Bu), 1.06 (t, 3H, $^3J_{H,H}$ = 6.9, $CO_2CH_2CH_3$) 1.28, 1.61 (each s, each 9H, *t*Bu), 4.08–4.20 (m, 2H, $CO_2CH_2CH_3$), 6.97–6.98 (m, 8H, arom-H), 7.68 (d, 2H, $^3J_{H,H}$ = 6.9, arom-H).

^{13}C NMR (CD_2Cl_2): δ = 13.9 ($CO_2CH_2CH_3$), 29.8, 29.9, 30.9 [$C(CH_3)_3$], 31.9, 33.4, 37.1 [$C(CH_3)_3$], 61.9 ($CO_2CH_2CH_3$), 83.9 (C-6), 87.7 (C-5), 104.7 (C-1), 127.2, 128.1, 128.8 (C-arom), 128.9 (1-*ipso*-C), 129.9, 130.8 (C-arom), 134.9 (8-*ipso*-C), 144.4 (C-4), 158.3 (C-3), 165.0 ($CO_2CH_2CH_3$), 169.7 (C-7).

MS (EI, 70 eV): *m/z* (%) = 530 (31, M^+), 473 (3, $M^+ - C_4H_9$), 309 (33, $M^+ - C_{15}H_{27}N$), 221 (14, $C_{15}H_{27}N^+$), 180 (100, $M^+ - PhNCPh$), 105 (80, $M^+ - PhCO$), 77 (56, Ph^+), 57 (41, $C_4H_9^+$).

Anal calc for $C_{33}H_{42}N_2O_4$, 530.71: C, 74.69; H, 7.98; N, 5.28. Found: C, 74.5; H, 8.2; N, 5.3.

Synthesis of ***17a,b****: general procedure*

The procedure was carried out as described for **16a** except for the purification which was performed on silica gel using *n*-pentane/diethyl ether (10:1) as eluent.

- *Ethyl 2-(benzoyloxy)-2-(2,3,4-tri-tert-butyl-1,2-dihydroazet-2-yl)-2-[(phenylamino)carbonyl] acetate* ***17a***

From **1** (0.51 g, 2.3 mmol) and **15a** (0.74 g, 2.4 mmol) to afford 0.81 g (64%) of **17a** as colorless crystals after recrystallization from diethyl ether at −20 °C. Mp 137 °C.

IR (CCl_4): ν = 3 356 (N–H), 2 973, 1 727 (C=O), 1 699 (C=O), 1 601 (C=O), 1 549, 1 498, 1 445, 1 313, 1 278 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.92 (s, 9H, *t*Bu), 1.11 (t, 3H, $^3J_{H,H}$ = 7.4, $CO_2CH_2CH_3$), 1.22, 1.24 (each s, each 9H, *t*Bu), 3.02 (s, 1H, NH), 3.01–4.03 (m, 1H, $CO_2CH_2CH_3$), 4.22 (dq, 1H, $^2J_{H,H}$ = 10.8, $^3J_{H,H}$ = 7.4, $CO_2CH_2CH_3$), 6.94 (t, 1H, $^3J_{H,H}$ = 7.4, arom-H), 7.18 (t, 2H, $^3J_{H,H}$ = 7.4, arom-H), 7.37 (t, 2H, $^3J_{H,H}$ = 7.9, arom-H), 7.49 (t, 1H, $^3J_{H,H}$ = 7.9, arom-H), 7.55 (d, 2H, $^3J_{H,H}$ = 7.6, arom-H), 8.04 (d, 2H, $^3J_{H,H}$ = 7.1, arom-H), 10.11 (s, 1H, N–H).

^{13}C NMR ($CDCl_3$): δ = 13.3 ($CO_2CH_2CH_3$), 28.9, 29.3, 32.1 [$C(CH_3)_3$], 31.1, 33.2, 38.2 [$C(CH_3)_3$], 62.2 ($CO_2CH_2CH_3$), 77.5 (C-2), 87.2 (C-4′), 119.1, 123.4, 128.9, 129.8 (C-arom), 129.9 (CO-*ipso*-C), 133.1 (C-arom), 135.8 (C-3′), 138.5 (s, N-*ipso*-C), 156.7 (C-2′), 161.3 (C-3), 165.2 (OCOPh), 170.0 (C-1).

MS (EI, 70 eV): *m/z* (%) = 548 (75, M^+), 533 (94, $M^+ - C_4H_9$), 222 (8, $C_{15}H_{27}NH^+$), 105 (100, $PhCO^+$), 77 (32, Ph^+), 57 (21, $C_4H_9^+$).

Anal calc for $C_{33}H_{42}N_2O_5$, 548.73: C, 72.23; H, 8.08; N, 5.11. Found: C, 71.7; H, 7.5; N, 5.3.

- *Ethyl 2-(2,3,4-tri-tert-butyl-1,2-dihydroazet-2-yl)-2-(4-methoxybenzoyloxy)-2-[(phenylamino)carbonyl]-acetate* ***17b***

From **1** (0.55 g, 2.5 mmol) and **15b** (0.88 g, 2.6 mmol) to afford 0.98 g (68%) of **17b** as colorless crystals after recrystallization from diethyl ether at −20 °C. Mp 141 °C.

IR (CCl_4): ν = 3 358 (N–H), 2 960, 1 724 (C=O), 1 697 (C=O), 1 604 (C=O), 1 549, 1 498, 1 445, 1 313, 1 278 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.90 (s, 9H, *t*Bu), 1.18 (t, 3H, $^3J_{H,H}$ = 7.4, $CO_2CH_2CH_3$), 1.28, 1.31 (each s, each 9H, *t*Bu), 3.03 (s, 1H, NH), 3.98–4.11 (m, 1H, $CO_2CH_2CH_3$), 4.29 (dq, 1H, $^2J_{H,H}$ = 10.7, $^3J_{H,H}$ = 7.2, $CO_2CH_2CH_3$), 6.93 (d, 2H, $^3J_{H,H}$ = 9.1, arom-H), 7.01 (t, 1H, $^3J_{H,H}$ = 7.4, arom-H), 7.25 (t, 2H, $^3J_{H,H}$ = 7.4, arom-H), 7.61 (d, 2H, $^3J_{H,H}$ = 7.4, arom-H), 8.05 (d, 2H, $^3J_{H,H}$ = 9.1, arom-H), 10.11 (s, 1H, N–H).

^{13}C NMR (CD_2Cl_2): δ = 13.3 ($CO_2CH_2CH_3$), 28.9, 29.3 [$C(CH_3)_3$], 31.1 [$C(CH_3)_3$], 32.1 [$C(CH_3)_3$], 33.1, 38.2 [$C(CH_3)_3$], 55.4 (OCH_3), 62.1 ($CO_2CH_2CH_3$), 77.5 (C-2), 86.8 (C-4′), 113.7 (C-arom), 119.0 (*para*-C), 122.4 (CO-*ipso*-C), 123.1, 128.7, 131.9 (C-arom), 135.9 (C-3′), 138.7 (s, N-*ipso*-C), 156.9 (C-2′), 161.3 (C-3), 163.6 (*para*-C-OMe), 164.9 ($OCOC_6H_4OCH_3$), 170.3 (C-1).

MS (EI, 70 eV): *m/z* (%) = 578 (11, M^+), 533 (17, $M^+ - CH_3$), 222 (4, $C_{15}H_{27}NH^+$), 135 (100, $MeOC_6H_4CO^+$), 77 (13, Ph^+), 57 (30, $C_4H_9^+$).

Anal calc for $C_{34}H_{46}N_2O_6$, 578.74: C, 70.56; H, 8.01; N, 4.84. Found: C, 70.2; H, 7.9; N, 4.8.

Thermolysis of ***17***

A solution of **17a** (0.3 g, 0.55 mmol) or **17b** (0.3 g, 0.52 mmol) in toluene (20 mL) was heated at 150 °C for 24 h with magnetic stirring in a Schlenk pressure tube. After evaporation of the solvent under vacuum (20 °C/0.001 mbar) a yellow oil was obtained. Purification by column chromatography on silica gel using *n*-pentane/diethyl ether (10:1) furnished 0.07 g (0.17 mmol, 31%, from **17a**) or 0.14 g (0.33 mmol, 64%, from **17b**) of 2-ethoxycarbonyl-2-[(phenylamino)carbonyl]-3,4,5-tri-*tert*-butyl-2*H*-pyrazole **18** as a colorless solid.

IR (CCl_4): ν = 3 480 (N–H), 2 957, 1 717 (C=O), 1 687 (C=O), 1 593, 1 488, 1 484, 1 302, 1 220.

^1H NMR ($CDCl_3$): δ = 0.80 (s, 9H, *t*Bu), 1.24 (t, 3H, $^3J_{H,H}$ = 7.4, $CO_2CH_2CH_3$), 1.26, 1.30 (each s, each 9H, *t*Bu), 3.54 (m, 2H, $CO_2CH_2CH_3$), 6.05 (s, 1H, NH), 6.86 (d, 2H, $^3J_{H,H}$ = 7.4, arom-H), 6.98 (t, 1H, $^3J_{H,H}$ = 7.4, arom-H), 7.19 (d, 2H, $^3J_{H,H}$ = 7.7, arom-H).

^{13}C NMR (CD_2Cl_2): δ = 13.3 ($CO_2CH_2CH_3$), 27.4, 27.6, 28.3 [$C(CH_3)_3$], 35.7, 36.3, 39.2 [$C(CH_3)_3$], 60.4 ($CO_2CH_2CH_3$), 78.2 (C-2), 120.4, 123.1, 128.2 (C-arom), 135.0 (*ipso*-C), 150.1 (C-4), 161.6 (CO_2Et), 162.1 (C-3), 177.6 (N–C=O), 183.3 (C-5).

MS (EI, 70 eV): *m/z* (%) = 426 (11, M^+), 369 (94, $M^+ - C_4H_9$), 341 (33, $M^+ - CCO_2Et$), 258 (22, $M^+ - C_4H_9CNCO_2Et$), 77 (12, Ph^+), 57 (100, $C_4H_9^+$).

Anal calc for $C_{26}H_{38}N_2O_3$, 426.60: C, 73.20; H, 8.98; N, 6.57. Found: C, 72.0; H, 8.8; N, 6.5.

Synthesis of N-[α-(4,5,6-tri-tert-butyl-1-aza-3-oxabicyclo[2.2.0]hex-5-en-2-ylidene)benzyl]-N-methylbenzamide ***20***

A solution of **1** (0.44 g, 2.0 mmol) and **19** (0.50 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was heated for 48 h at 75 °C with magnetic stirring in a Schlenk pressure tube. After evaporation of the solvent under vacuum (20 °C/0.001 mbar) a yellow oil was obtained. Purification by column chromatography on silica gel using *n*-pentane/diethyl ether as eluent (after starting with *n*-pentane, diethyl ether was added successively in 1 mL portions until the yellow product began to move) gave 0.89 g (95%) of **20** as a yellow solid that was recrystallized from *n*-pentane. Compound **20** was obtained as a mixture of *E*- and *Z*-isomers; the isomer ratio as determined by ^1H NMR spectroscopy was 60(**A**):40(**B**) but **A** and **B** could not be assigned to the *E* and *Z* configurations.

IR (CCl_4): ν = 2 962, 2 920, 1 678 (C=O), 1 648, 1 464, 1 392 cm^{-1}.

^1H NMR (**A**) ($CDCl_3$): δ = 0.80, 1.08, 1.14 (each s, each 9H, *t*Bu), 3.09 (s, 3H, N–CH_3), 6.94–7.41 (m, 8H, arom H), 7.61, 7.71 (each d, each 1H, arom H).

^1H NMR (**B**) ($CDCl_3$): δ = 0.91, 1.15, 1.28 (each s, each 9H, *t*Bu), 3.36 (s, 3H, N–CH_3), 6.94–7.41 (m, 8H, arom H), 7.61, 7.71 (each d, each 1H, arom H).

^{13}C NMR (**A**) (CD_2Cl_2): δ = 25.0, 29.5, 30.7 [C(CH_3)$_3$], 31.0, 34.0, 35.8 [C(CH$_3$)$_3$], 34.1 (N–CH_3), 106.1 (C-2-*C*PhN), 109.3 (C-4), 124.7–129.3 (C-arom), 136.7 (*ipso*-C), 140.6 (C-5), 159.1 (C-2), 163.3 (C-6), 172.7 (N–*C*=O).

^{13}C NMR (**B**) (CD_2Cl_2): δ = 25.0, 29.4, 30.8 [C(CH_3)$_3$], 31.3, 33.6, 34.9 [C(CH$_3$)$_3$], 36.6 (q, N–CH_3), 108.2 (C-2-*C*PhN), 110.0 (C-4), 124.7–129.3 (C-arom), 136.1 (*ipso*-C), 140.8 (C-5), 158.6 (C-2), 164.8 (C-6), 173.1 (N–*C*=O).

MS (EI, 70 eV): m/z (%) = 472 (17, M^+), 457 (13, M^+ – CH_3), 251 (40, M^+ – CCO_2Et), 118 (100, PhCON – H^+), 105 (40, $PhCO^+$), 77 (13, Ph^+), 57 (38, $C_4H_9^+$).

Anal calc for $C_{31}H_{40}N_2O_2$, 472.67: C, 78.78; H, 8.53; N, 5.92. Found: C, 78.9; H, 8.5; N, 5.8.

Synthesis of 2,3-diphenyl-5,6,7-tri-tert-butyl-1-aza-4-thiabicyclo[3.2.0]hepta-2,6-diene **23**

A solution of **1** (0.44 g, 2.0 mmol) and **22** (0.54 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was heated for 48 h at 75 °C with magnetic stirring in a Schlenk pressure tube. After evaporation of the solvent under vacuum (20 °C/0.001 mbar) a yellow oil was obtained. Purification by column chromatography on silica gel using *n*-pentane/diethyl ether as eluent (after starting with *n*-pentane diethyl ether was added successively in 1 mL portions until the light yellow product began to move) gave 0.13 g (15%) of **23** as a yellow solid that was recrystallized from $CHCl_3$.

IR (CCl_4): ν = 2 955, 2 869, 1 597 (C=O), 1 481, 1 392, 1 386, 1 362 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.96, 1.26, 1.33 (each s, each 9H, *t*Bu), 6.79–7.25 (m, 10H, arom-H).

^{13}C NMR (CD_2Cl_2): δ = 26.2, 30.4 [C(CH_3)$_3$], 31.6 [C(CH$_3$)$_3$], 31.8 [C(CH_3)$_3$], 31.8, 33.2 [C(CH$_3$)$_3$], 93.5 (C-5), 126.7, 127.2 (C-arom), 127.5 (C-3), 127.7, 128.0, 129.7 (C-arom), 135.1 (*ipso*-C), 135.5 (C-2), 136.2 (*ipso*-C), 142.3 (C-6), 161.7 (C-7).

MS (EI, 70 eV): m/z (%) = 431 (78, M^+), 374 (67, M^+ – C_4H_9), 293 (100, M^+ – $C_{10}H_{18}$), 57 (4, $C_4H_9^+$).

Anal calc for $C_{29}H_{37}NS$, 431.68: C, 80.69; H, 8.64; N, 3.24. Found: C, 79.1; H, 8.3; N, 3.1.

Crystal data and summary of data collection parameters for **17b** *and* **23**

Intensity measurements were carried out for both products with a Siemens P4 diffractometer using Mo-K_α radiation at room temperature. The structures were solved by direct methods with SHELXS-86 [32] and refined by full-matrix least-squares methods by SHELXL-93 [33]. Hydrogen atoms were placed in the calculated positions (d_{C-H} = 0.960 Å) and all other atoms were refined anisotropically.

17b: crystal size: 0.35 × 0.25 × 0.15 mm^3; monoclinic $P2_1/n$; a = 17.790(2) Å, b = 13.044(1) Å, c = 17.558(2) Å, β = 116.27(1)°; V = 3242.9(6) $Å^3$; Z = 4; d_{calc} = 1.185 Mg m^{-3}; μ = 0.081 mm^{-1}; $F(000)$ = 1248; Θ range 1.45–25.00°; 6993 measured reflections were reduced to 5715 independent reflections (R_{int} = 0.0348). The final refinement with 380 parameters converged with R_1 = 0.0707; wR_2 = 0.1272 [observed data, $I > 2\sigma(I)$] and R_1 = 0.1745, wR_2 = 0.1733 (all data) with $w^{-1} = [\sigma^2(F_o^2) + (0.0356P)^2 + 0.5479P]$ and $P = [F_o^2 + 2F_c^2]/3$; residual electron density 266 e nm^{-3} and −233 e nm^{-3}; GOF on F^2 1.262.

23: crystal size: 0.35 × 0.26 × 0.20 mm^3; monoclinic $P2_1/c$; a = 9.247(2) Å, b = 15.524(3) Å, c = 18.075(3) Å, β = 99.42(2)°; V = 2559.7(8) $Å^3$; Z = 4; d_{calc} = 1.120 Mg m^{-3}; μ = 0.142 mm^{-1}; $F(000)$ = 936; Θ range 1.74–22.50°; 4412 measured reflections were reduced to 3336 independent reflections (R_{int} = 0.0405). The final refinement with 280 parameters converged with R_1 = 0.0611; wR_2 = 0.1155 [observed data, $I > 2\sigma(I)$] and R_1 = 0.1195, wR_2 = 0.1365 (all data) with $w^{-1} = [\sigma^2(F_o^2) + (0.0396P)^2]$ and $P = [F_o^2 + 2F_c^2]/3$; residual electron density 238 e nm^{-3} and −235 e nm^{-3}; GOF on F^2 1.243.

Crystal data and summary of data collection parameters for **10d** *and Z-***20**

Intensity measurements were carried out for both products with an Imaging Plate Diffraction system (IPDS-STOE) using Mo-K_α radiation at room temperature. The structures were solved by direct methods with SHELXS-86 [32] and refined by full-matrix least-squares methods by SHELXL-93 [33]. Hydrogen atoms were placed in the calculated positions (d_{C-H} = 0.960 Å) and all other atoms were refined anisotropically.

10d: crystal size: 0.40 × 0.35 × 0.25 mm^3; monoclinic $P2_1/n$; a = 8.251(2) Å, b = 9.773(2) Å, c = 29.155(6) Å, β = 90.25(3)°; V = 2350.9(8) $Å^3$; Z = 4; d_{calc} = 1.038 Mg m^{-3}; μ = 0.061 mm^{-1}; $F(000)$ = 808; Θ range 2.51–28.23°; 31822 measured reflections were reduced to 5633 independent reflections (R_{int} = 0.1092). The final refinement with 245 parameters converged with R_1 = 0.0688; wR_2 = 0.1577 [observed data, $I > 2\sigma(I)$] and R_1 = 0.1331, wR_2 = 0.1804 (all data) with $w^{-1} = [\sigma^2(F_o^2) + (0.0571P)^2]$ and $P = [F_o^2 + 2F_c^2]/3$; residual electron density 299 e nm^{-3} and −340 e nm^{-3}; GOF on F^2 1.385.

Z-**20**: crystal size: 0.30 × 0.25 × 0.18 mm^3; monoclinic $P2_1/c$; a = 14.966(3) Å, b = 9.587(2) Å, c = 19.918(4) Å, β = 91.04(3)°; V = 2857.3(10) $Å^3$; Z = 4; d_{calc} = 1.099 Mg m^{-3}; μ = 0.068 mm^{-1}; $F(000)$ = 1024; Θ range 2.05–26.41°; 21886 measured reflections were reduced to 5486 independent reflections (R_{int} = 0.1231). The final refinement with 316 parameters converged with R_1 = 0.0696; wR_2 = 0.1692 [observed data, $I > 2\sigma(I)$] and R_1 = 0.1211, wR_2 = 0.1997 (all data) with $w^{-1} = [\sigma^2(F_o^2) + (0.0855P)^2 + 0.3364P]$ and $P = [F_o^2 + 2F_c^2]/3$; residual electron density 407 e nm^{-3} and −310 e nm^{-3}; GOF on F^2 1.385.

Supplementary material

Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° SUP 90478 and are available on request from the Document Supply Center.

Acknowledgments

We thank the Fonds der Chemischen Industrie for generous financial support of our work.

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