1,3-DIPOLAR CYCLOADDITION OF NITRILE OXIDES TO 8-AZAHEPTAFULVENES

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Abstract - Azaheptafulvenes (**2**) reacted readily with nitrile oxides (**1**) to give, as a rule, only adducts derived from a reaction involving the C=N moiety of **2**. The adducts consisted of a mixture of rapidly equilibrating "spiro" and "condensed" isomers, i.e. **6**⇌**8**, whose ratio was found to be dependent on substituents, temperature and solvent. The zwitterion (**7**) is an an appealing intermediate both for cycloaddition and isomerisation. Decomposition of the adducts to benzene, R^1CN and R^2NCO provided evidence in favor of the presence of the "norcaradiene" derivatives (**14**) (undetectable by nmr) in equilibrium with **6** and **8**. Only products arising from the "spiro" isomer (**6**) were obtained in high yields in the catalytic hydrogenation of **6/8**.

INTRODUCTION

Cyclic polyenes continue to attract considerable interest as ideal substrates for the study of periselectivity and site selectivity in cycloadditions.[1] Tropone has certainly played a leading role in this field.[2] As far as 1,3-dipolar cycloadditions are concerned, we found that the attack of benzonitrile oxide to the carbon-oxygen double bond of tropone prevails over that to the C_2-C_3 double bond while the [4+2] cycloaddition to the C_4-C_5 double bond and the [6+4] cycloaddition involving the whole cycloheptatriene moiety are minor reaction pathways.[3a] In the case of diphenylnitrile imine the attack to the carbon-oxygen double bond was not observed and the addition to the C_2-C_3 double bond was highly prevalent over those to the C_4-C_5 double bond and to the cycloheptatriene moiety (Scheme 1).[3b] The study of the reaction of diphenylnitrile imine with tropone imines, *i.e.*, 8-azaheptafulvenes, disclosed a dramatic change[4] in site selectivity as compared to tropone: only the attack by the carbon atom of diphenylnitrile imine to the nitrogen atom of azaheptafulvene took place and the reaction pathway ended up with the two kinetically controlled "condensed" adducts (**C**) and (**D**) (Scheme 2). This finding requires formation of the "spiro" adduct (**B**) as intermediate (never detected in the reaction mixtures either from cycloaddition or from decomplexation reactions) which can rearrange to both final adducts. One of the final adducts, *i.e.* (**C**), probably

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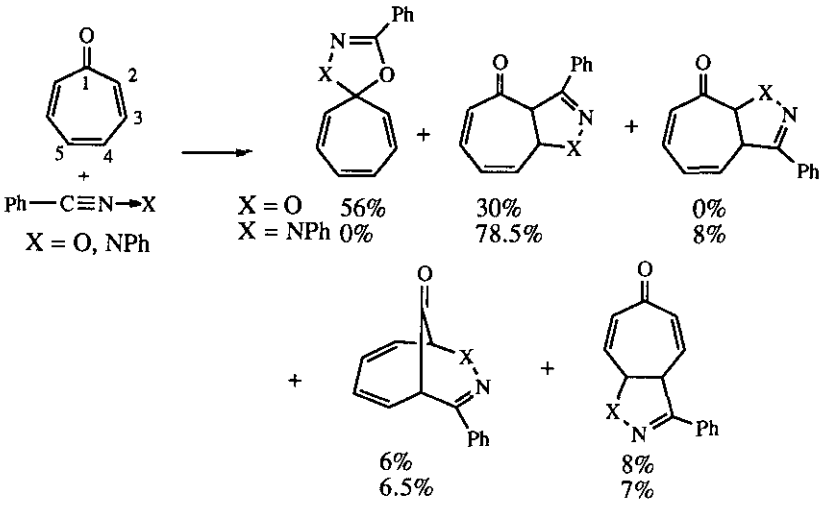
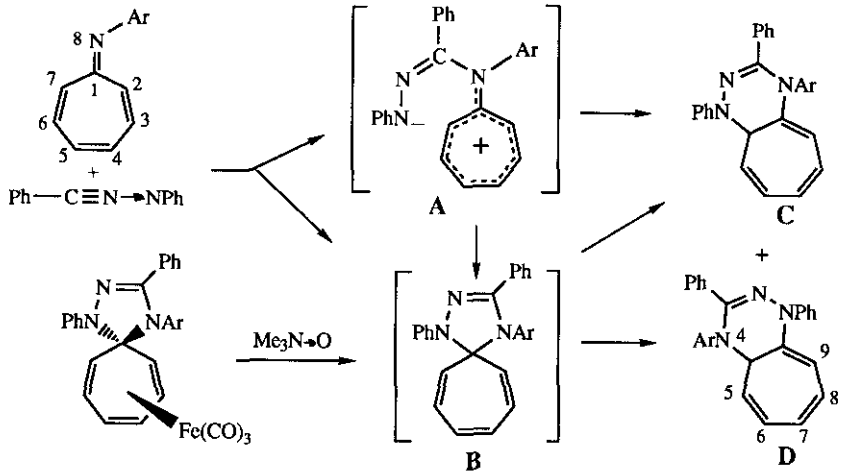
Dedicated to Prof. Rolf Huisgen on the occasion of his 75th birthday.



Scheme 1. Relative yields of the primary adducts of the reactions of benzonitrile oxide (X = O) and diphenylnitrile imine (X = NPh), respectively, with tropone.



Scheme 2

also arises directly from the dipolar intermediate (**A**) as suggested by the observation that the **C**/**D** ratio was always significantly higher in the cycloaddition than in the related decomplexation reaction.

A dipolar intermediate is an appealing intermediate in the reactions of azaheptafulvenes and can also be advanced for the [π8 + π2] cycloadditions of these polyenes with isocyanates, ketenes, carbon disulfide, sulfenes *etc.*.[1c,5]

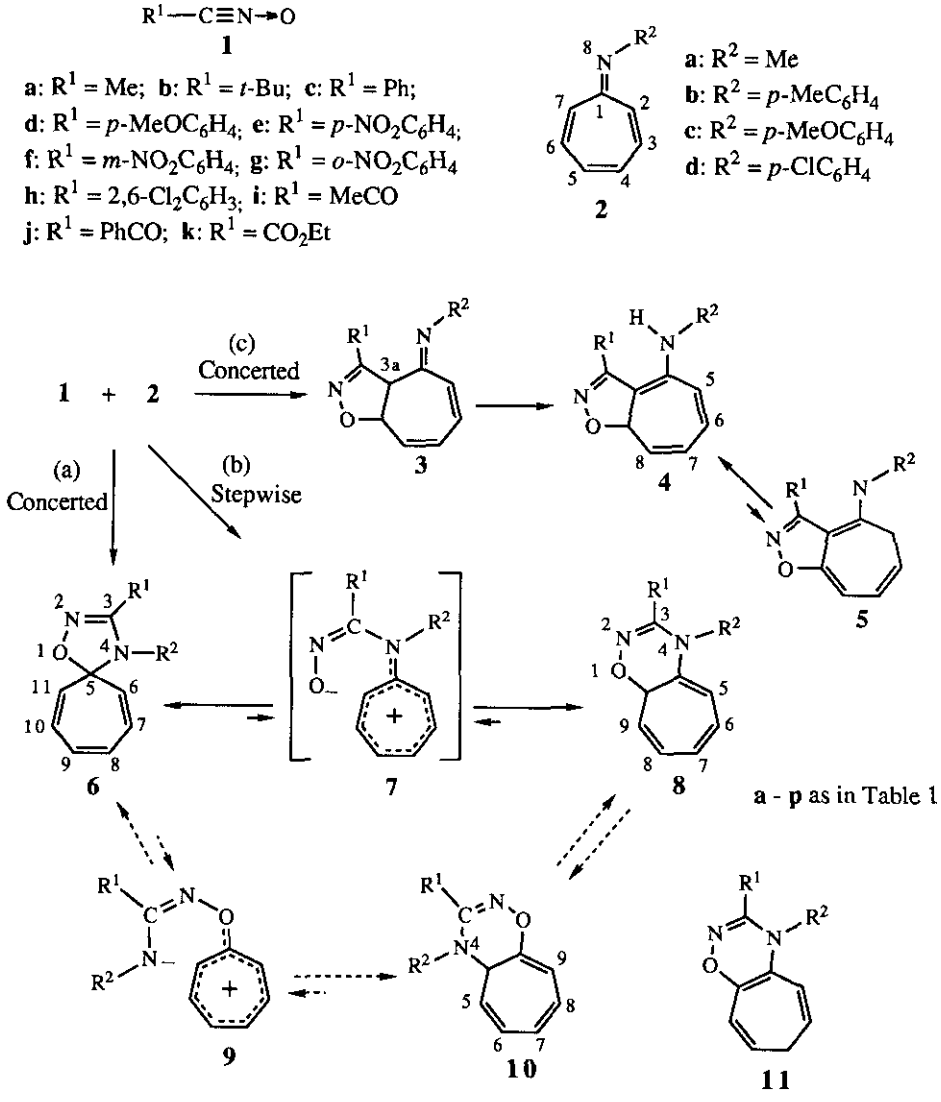
We also investigated the reaction of nitrile oxides with 8-azaheptafulvenes with the aim of finding out i) whether the reactivity of the C=N moiety [path (a) or (b), Scheme 3] of these dipolarophiles is so high to always overcome that of C=C bonds [path (c)] of the cycloheptatriene system, ii) whether the "condensed" form of the

adducts is intrinsically much more stable than the "spiro" form so that the former will always prevails over the latter no matter the type of heteroatom and the type of substituents present in the heterocyclic part of these compounds, iii) some evidence of the role played by zwitterionic intermediates in the cycloaddition as well as in the interconversion between the different forms of the adducts (Scheme 3). A recent report[6] on the reaction of aromatic nitrile oxides with *N*-arylazaheptafulvenes prompts us to disclose our results in this field.

CYCLOADDITION REACTIONS

Nitrile oxides (**1**), slowly generated in situ from the corresponding hydroximic acid chloride, with solid sodium carbonate or by slowly adding a solution of triethylamine, reacted readily with azaheptafulvenes (**2**)[7] in benzene at room temperature to give high yields of adducts (Scheme 3 and Table 1). In the case of the reaction of 2,2-dimethylpropanenitrile oxide (**1b**, R^1 = *t*-Bu) with 8-methyl (**2a**) and 8-*p*-tolylazaheptafulvene (**2b**) the ^{1}H nmr spectra as well as the ^{13}C nmr spectra showed that the addition product consisted of a single isomer, *i.e.*, the 1,2,4-oxadiazaspiro[4.6]undeca-2,6,8,10-tetraene derivatives (**6a**) and (**6b**), respectively. In fact, the ^{1}H nmr spectra displayed three multiplets, each corresponding to two vinyl protons [*e.g.*, **6b** (R^1 = *t*-Bu; R^2 = *p*-MeC_6H_4): ^{1}H Nmr δ (ppm, $CDCl_3$) 1.10 (s, Me_3C), 2.33 (s, Me), 5.89 (m, 2 H, H-6 and H-11, J = 11.0 Hz), 6.12 (m, 2 H, H-8 and H-9), 6.24 (m, 2 H, H-7 and H-10), 6.98 and 7.04 (AAXX' system of the *p*-tolyl group); ^{13}C nmr δ (ppm, $CDCl_3$) 21.0 (q, Me of the tolyl group), 26.7 (q, $\underline{Me}_3C$), 32.4 (s, $Me_3\underline{C}$), 98.9 (s, C-5), 126.5 (d, C-7 and C-10), 126.7 (d, C-6 and C-11), 129.0 (d, C-8 and C-9), 128.9, 131.8, 134.7 and 138.0 (d, d, s and s, aromatic carbons), 160.5 (s, C-3)], while the ^{13}C nmr spectra exhibited, in addition to the three doublets of the vinyl carbons, a singlet at ≈ 99 ppm, which is diagnostic of the presence of a quaternary carbon (C-5) bearing two heteroatoms. Thus, the "spiro" isomer (**6**), which was not detectable in the reaction of diphenylnitrile imine with azaheptafulvenes,[4] was the only isomer observed in the reaction mixtures of 2,2-dimethylpropanenitrile oxide (**1b**) with **2a** and **2b**, respectively.

However, the missing isomers, *i.e.*, the 4,9a-dihydrocyclohepta-1,2,4-oxadiazine derivatives (**8a**) and (**8b**) ("condensed" isomers), most probably were present in quantities just below the detection limits of the nmr techniques. In fact, the addition products of the reaction of acetonitrile oxide (**1a**, R^1 = Me) with the same azaheptafulvenes (**2a**) (R^2 = Me) and (**2b**) (R^2 = *p*-MeC_6H_4), respectively, exhibited only one spot on tlc but nmr spectra [*e.g.*, **6j** (R^1 = R^2 = Me): ^{1}H Nmr δ (ppm, CD_3CN) 1.80 (s, MeC), 2.52 (s, MeN), 5.80 (m, H-6 and H-11), 6.51 (m, H-7, H-8, H-9 and H-10); ^{13}C nmr δ (ppm, $CDCl_3$) 9.0 (q, MeC), 27.7 (q, MeN), 96.9 (s, C-5), 125.1 (d, C-6 and C-11), 127.2 and 129.4 (two d, C-7, C-8, C-9 and C-11), 151.9 (s, C-3). **8j**: ^{1}H Nmr δ (ppm, CD_3CN) 2.03 (s, MeC), 3.11 (s, MeN), 3.49 (ddd, H-9a, $J_{5,9a}$ = 1.1 Hz, $J_{8,9a}$ = 1.7 Hz and $J_{9,9a}$ = 5.0 Hz), 5.63 (br d, H-5, $J_{5,6}$ = 6.6 Hz), 5.72 (ddddd, H-9, $J_{5,9}$ = $J_{6,9}$ = $J_{7,9}$ = 0.7 Hz, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 5.0 Hz), 6.20 (ddd, H-8, $J_{7,8}$ = 5.7 Hz, $J_{8,9}$ = 9.5 Hz and $J_{8,9a}$ = 1.7 Hz), 6.51 (ddd, H-7, $J_{6,7}$ = 11.0 Hz, $J_{7,8}$ = 5.7 Hz and $J_{7,9}$ = 0.7 Hz), 6.58 (ddd, H-6, $J_{5,6}$ = 6.6 Hz, $J_{6,7}$ = 11.0 Hz and $J_{6,9}$ = 0.7 Hz). ^{13}C nmr δ (ppm, $CDCl_3$) 17.2 (q, MeC), 33.0 (q, MeN), 73.1 (d, C-9a), 96.6 (d, C-5), 121.7 (d, C-9), 124.1 (d,



Scheme 3

C-8), 126.9 (d, C-7), 129.0 (d, C-6), 130.3 (s, C-4a), 151.5 (s, C-3)] showed that they consisted of an inseparable mixture of "spiro" and "condensed" isomers, in which these latters (**8j** and **8k**, respectively) were either clearly dominant over or at least present in similar amounts to the formers (**6j** and **6k**, respectively). Diagnostic features of the "condensed" form **8** were the presence in the ^{1}H nmr spectra of five signals due to five vinyl protons [the highest field of which (at δ 5.63 in **8j**) could safely be attributed to H-5 which occupies a shielded β-enaminic position] and of a signal (at δ 3.49 in **8j**) assignable to H-9a, bonded to a saturated carbon but deshielded by the geminal oxygen atom. The deshielding effect of the oxygen atom and the shielding effect of the enamino group are also clearly reflected in the chemical shifts of C-9a [δ 73.1 in **8j**)] and C-5 [δ 96.6 in **8j**)],

Table 1. Total yields of the reactions of **1** with **2** in benzene and ratios (%) between the "spiro" (**6**) and the "condensed" isomers (**8**) in C_6D_6[a] and in CD_3CN at 20 °C.

	R^1	R2	Total yields(%)	C_6D_6 **6/8**	CD_3CN **6/8**
a	*t*-Bu	Me	60	100:0	100:0
b	*t*-Bu	*p*-MeC_6H_4	65	100:0	100:0
c	Ph	*p*-ClC_6H_4	90	95:5	
d	Ph	*p*-$MeOC_6H_4$	92	93:7	
e	Ph	*p*-MeC_6H_4	91	92:8	
f	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	85	92:8	
g	*p*-$NO_2C_6H_4$	*p*-MeC_6H_4	88	90:10	
h	*m*-$NO_2C_6H_4$	*p*-MeC_6H_4	86	88:12	92:8
i	*o*-$NO_2C_6H_4$	*p*-MeC_6H_4	70	<20:80[b]	50:50
j	Me	Me	50	10:90	47:53
k	Me	*p*-MeC_6H_4	80	30:70	58:42
l	Ph	Me	55	30:70	44:56
m	2,6-$Cl_2C_6H_3$	Me	75	6:94	12:88
n	MeCO	*p*-MeC_6H_4	76	59:41[c,d]	
o	PhCO	*p*-MeC_6H_4	75	48:52[e]	
p	COOEt	*p*-MeC_6H_4	78	50:50[e]	

[a]Ratios in $CDCl_3$ are, as a rule, similar to those in C_6D_6. [b]See EXPERIMENTAL. [c]In C_7D_8 at - 40 °C. [d]**6n/8n** = 80:20 in CD_2Cl_2 at - 70 °C. [e]In CD_2Cl_2 at - 50 °C

respectively.

In all examples reported in Table 1 but Entries **a** and **b** we could detect the presence of both the isomers (**6**) and (**8**) (see also next section for a discussion about the equilibrium between **6** and **8**). In contrast to our results, formation of a single "spiro" isomer was recently reported[6] for the reaction of benzonitrile oxide (**1c**) with azaheptafulvenes (**2b-d**) and of **1d** with **2b** (Entries **c-f**, Table 1): we feel that the small amounts of the "condensed" form present in these reactions and the fact that the ^1H nmr signals (in $CDCl_3$) of this isomer are broad led these authors, most probably, to overlook the presence of **8c-f** in equilibrium with **6c-f**.

It should also be stressed that we were able to detect only one "condensed" form, *i.e.*, **8**, in equilibrium with the "spiro" isomer (**6**). The nmr data (see above and the experimental section) are much more consistent with structure (**8**) than with structure (**10**). For example, the singlet at δ 130.3 is assignable to the N<u>C</u>=C (C-4a) carbon of **8j** but it is at too high a field for the O<u>C</u>=C carbon (C-9a) of **10j**. Moreover, the proton and the carbon

atom at position 4a of compounds (**10**) should absorb at fields very similar to those of the same nuclei at the same position of compounds (**D**) of Scheme 2. But H-4a and C-4a of **D** resonate at $\delta \leq 2.9$ and $\delta \leq 57$,[4] respectively, i.e. at higher fields by at least 0.6 ppm and 16 ppm than H-9a ($\delta \geq 3.5$) and C-9a ($\delta \geq 73$) of compounds (**8**). The absence of compound (**10**) in equilibrium with **6** and **8** suggest that zwitterion (**9**) is, as expected, definitely less stable than zwitterion (**7**) (Scheme 3). Attempts to induce the rearrangement to **10** by heating the equilibrating **6**⇌**8** mixture above room temperature led to decomposition of the adducts to benzene, R^1CN and R^2NCO (see below). In some cases, e.g. **6c/8c** (R^1 = Ph, R^2 = *p*-ClC_6H_4) and **6h/8h** (R^1 = *m*-$NO_2C_6H_4$, R^2 = *p*-MeC_6H_4), decomposition was accompanied by isomerisation to a new compound for which structure **11** has recently been suggested.[6]

The reactions between nitrile oxides and azaheptafulvenes, whose results are gathered in Table 1, were clean reactions and no significant amounts of other adducts, in addition to **6** and **8**, could as a rule be detected. This means that the reaction of **1** with **2** involving the C=N moiety is at least ≥ 2 kcal mol^{-1} more favored than attacks of **1** to the carbon-carbon double bonds of **2**.

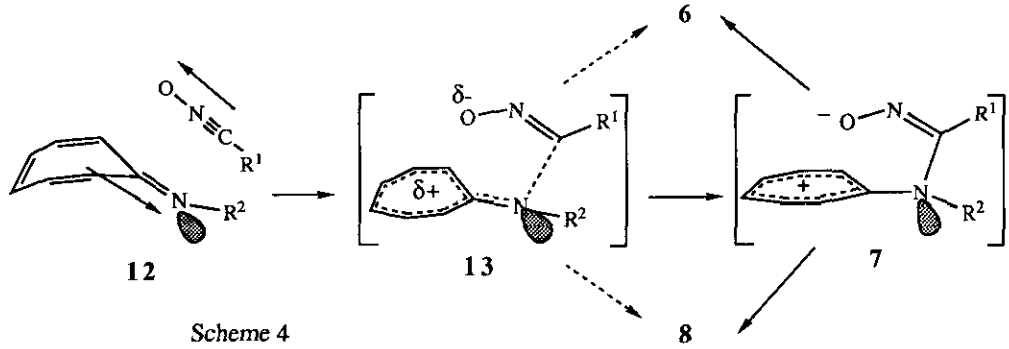
Anyway, at least in one case, *i.e.*, the reaction of acetonitrile oxide (**1a**) with **2b** in benzene, we managed to isolate ≈ 3% yield of an orange-yellow product resulting from attack of the nitrile oxide to C_6-C_7 (or C_2-C_3) bond of **2b**. The orange-yellow color suggested the presence in this compound of a highly conjugated system. The ^1H nmr spectrum did not display any signal attributable to H-3a of adduct (**3k**) (R^1 = Me; R^2 = *p*-MeC_6H_4), but there was a broad signal at δ 5.70 which exchanged with D_2O. The most straightforward way to rationalize these observations is to assume a tautomerization of the primary adduct (**3k**) to **4k** (Scheme 3). All the other ^1H nmr signals were in keeping with structure (**4k**) [^1H nmr δ (ppm, $CDCl_3$) 2.20 (s, Me), 2.30 (s, Me), 4.98 (dd, H-8a, $J_{7,8a}$ = 2.4 Hz and $J_{8,8a}$ = 2.6 Hz), 5.70 (br s, NH), 5.67 (dddd, H-8, $J_{5,8}$ = 1.0 Hz, $J_{6,8}$ = 0.8 Hz, $J_{7,8}$ = 10.0 Hz and $J_{8,8a}$ = 2.6 Hz), 6.10 (dddd, H-7, $J_{5,7}$ = 1.0 Hz, $J_{6,7}$ = 5.5 Hz, $J_{7,8}$ = 10.0 Hz and $J_{7,8a}$ = 2.4 Hz), 6.51 (ddd, H-5, $J_{5,6}$ = 12.0 Hz and $J_{5,7}$ = $J_{5,8}$ = 1.0 Hz), 6.61 (ddd, H-6, $J_{5,6}$ = 12.0 Hz, $J_{6,7}$ = 5.5 Hz and $J_{6,8}$ = 0.8 Hz), 6.68 and 7.03 (two m, 4 H, AAXX' system of the *p*-tolyl group)]. In addition to the signals of **4k** other low intensity signals [^1H nmr δ (ppm, $CDCl_3$) 3.40 (d, 2 H, J = 6.1 Hz), 5.35 (dt, 1 H, J = 6.1 Hz and 9.5 Hz), 5.93 (d, 1 H, J = 6.5 Hz), the two latter protons are coupled to a proton buried under H-7 of **4k** at ≈ δ 6.1] suggested the presence of an isomer of **4k** in which a methylene group is coupled to only one vinyl proton as, for example, in **5k**. Preliminary results, on which we will report soon, show that formation of adducts to the C_6-C_7 bond always accompanies the dominant adducts (**6/8**) in the reaction of *o*,*o*'-disubstituted benzonitrile oxides and 8-aryl-8-azaheptafulvenes in apolar solvents (*i.e.*, benzene and cyclohexane).

When the reaction of acetonitrile oxide with **2b** was carried out in methanol the formation of **4k** was suppressed, suggesting that the TS of the attack to the C=N moiety is much more polar than that to the C=C bond. Further evidence that the TS of attack to the C=N moiety of **2** is more polar than a "bona fide" concerted 1,3-dipolar cycloaddition to a carbon-carbon double bond was provided by competition experiments. Benzonitrile oxide **1c** (R^1 = Ph) was reacted with an excess mixture of *N*-phenylmaleimide and azaheptafulvene (**2c**) (R^2 = *p*-

$MeOC_6H_4$) in benzene and acetonitrile, respectively. The relative rate of the reaction of **1c** with **2c** with respect to that of **1c** with *N*-phenylmaleimide increased from 0.80 in benzene to 3.50 in acetonitrile. This is certainly not a dramatic effect but it clearly testifies that on going from the educts to the TS, in the reaction of nitrile oxides with azaheptafulvenes, there is a significant increase in polarity (dipole moment) as a result of a substantial development of a negative charge on the nitrile oxide moiety and of a positive charge on the cycloheptatriene residue. In fact, it should be stressed that on the way to the TS the dipole moments of the nitrile oxide [μ = 4.00 D (experimental) for **1c**][8] and of **2** [$\mu \approx$ 2.0 D for **2a** (semiempirical calculations)][9,10] certainly must adopt an almost antiparallel orientation (as in **12**, Scheme 4) which should bring about a significant decrease in the dipole moment of the TS as compared to the educts; only a strong development of partial charges (see **13**, Scheme 4) can contrast and reverse this tendency. Elegant and convincing evidence of the presence of these charge has also been provided by Saito *et al.* through a Hammett correlation for the reaction of *p*-substituted benzonitrile oxides with **2b** (ρ = +0.99).[6]

It is quite obvious that it is not possible on the basis of these data to choose between a two step process *via* dipolar intermediate (**7**) and a highly asynchronous one step process in which TS (**13**) directly collapse to **6** or to **8** (Scheme 4). The stability of a tropylium ion, further enhanced in the case of **7** by conjugation with the lone pair, along with the fact that a negative charge is certainly well accepted on an oxime system (in particular when R^1 is an electron attracting groups such as COR) makes it very tempting to suggest that , at least in the case of electron poor nitrile oxides, **7** is an intermediate in the formation of the adducts. In the next section it will be shown that formation of **7** from **6** and **8** is, indeed, a very easy and fast process.

Scheme 4 roughly describes the approach of the nitrile oxides to azaheptafulvenes [whose "tub" structure is more stable (by 2-3 kcal mol^{-1} in the case of **2a**) than planar conformation according to semiempirical MO calculations][10] to give the oriented complex (**12**) and then TS (**13**): we suggest that the "nucleophilic" attack to the carbon atom of the nitrile oxide by the nitrogen atom of azaheptafulvene involves the π system of this latter and not the nitrogen lone pair: the MO attributable to this lone pair is about 1 eV lower in energy than the π-HOMO.[10] The coefficient at the nitrogen in the HOMO of **2a** is much larger than that at C-1[10] once again suggesting, in the context of FO theory and reasonably assuming a dominant HO_2-$LU_{1,3\text{-dipole}}$ interaction, a very



Scheme 4

asynchronous bond formation in **13.** We hope that MO calculations will help us in the next future to choose between concerted and stepwise processes in these borderline reactions. To date, only Huisgen has been able to convincingly document and prove, on an experimental basis, a "beyond doubt" stepwise 1,3-dipolar cycloaddition.[11]

EQUILIBRIUM BETWEEN "SPIRO" AND "CONDENSED" ISOMERS, *i.e.*, **6** $\rightleftharpoons$ **8**.

All the reactions studied but those of 2,2-dimethylpropanenitrile oxide (see Table 1) afforded an inseparable mixture (one spot on tlc) of **6** and **8.** As a matter of fact, compounds (**6**) and (**8**) were converted into each other very readily and equilibration rate was enhanced by an increase both in solvent polarity and in the electron attracting power of the substituent at position 3 (*i.e.*, of the R^1 group) as shown by nmr data.

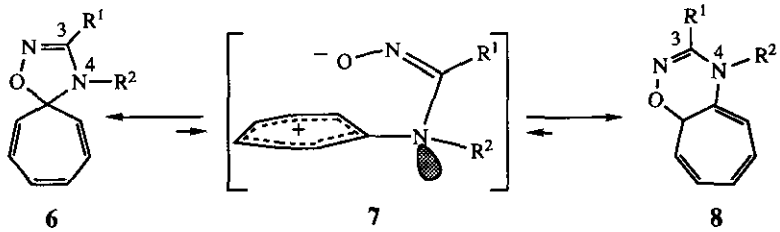
Derivatives with a methyl group at position 3 or at position 4, *i.e.*, Entries **j**, **k**, **l** and **m** of Table 1, exhibited the lowest interconversion rate. In fact, the ^{1}H nmr spectra of the mixtures (**6j/8j**) ($R^1 = R^2 =$ Me), (**6k/8k**) ($R^1 =$ Me; $R^2 = p$-MeC_6H_4) and (**6m/8m**) ($R^1 = 2,6$-$Cl_2C_6H_4$; $R^2 =$ Me) at 20° in C_6D_6, $CDCl_3$ and CD_3CN, respectively, displayed well resolved signals for both the isomers [e.g., **6m**: ^{1}H Nmr δ (ppm, CD_3CN) 2.88 (s, MeN), 6.01 (m, H-6 and H-11), 6.56 (m, H-7, H-8, H-9 and H-10), 7.4-7.6 (aromatic protons). **8m**: ^{1}H Nmr δ (ppm, CD_3CN) 2.88 (s, MeN), 3.60 (ddd, H-9a, $J_{5,9a}$ = 1.0 Hz, $J_{8,9a}$ = 1.7 Hz and $J_{9,9a}$ = 5.0 Hz), 5.78 (br d, H-5, $J_{5,6}$ = 6.5 Hz), 5.93 (ddddd, H-9, $J_{5,9} = J_{6,9} = J_{7,9}$ = 0.7 Hz, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 5.0 Hz), 6.29 (br ddd, H-8, $J_{7,8}$ = 5.5 Hz, $J_{8,9}$ = 9.5 Hz and $J_{8,9a}$ = 1.7 Hz), 6.62 (br dd, H-7, $J_{6,7}$ = 11.0 Hz and $J_{7,8}$ = 5.5 Hz), 6.78 (ddd, H-6, $J_{5,6}$ = 6.5 Hz, $J_{6,7}$ = 11.0 Hz and $J_{6,9}$ = 0.7 Hz) 7.4-7.6 (aromatic protons)] and no relevant spin saturation transfer effects could be detected at this temperature in these solvents. Thus, for these compounds equilibration at room temperature was slow on the nmr time scale. However, also for these compounds equilibration takes place quite rapidly as demonstrated (see next section) by the observation that compound (**6k/8k**) could be hydrogenated catalytically at room temperature to give high yields of products arising only from the "spiro" form (**6k**) notwithstanding dominance of the "condensed" isomer (**8k**).

Also in the case of **6l/8l** (R^1 = Ph; R^2 = Me) a well resolved spectrum was obtained in C_6D_6 at 20 °C and irradiation experiments induced a negligible spin saturation transfer. However, passing to CD_3CN [**6l/8l** = 44:56 at 20 °C. **6l**: ^{1}H Nmr δ (ppm, CD_3CN) 2.56 (s, MeN), 5.97 (m, H-6 and H-11), 6.54 (m, H-7, H-8, H-9 and H-10), 7.35-7.6 (aromatic protons). **8l**: ^{1}H Nmr δ (ppm, CD_3CN) 3.00 (s, MeN), 3.72 (ddd, H-9a, $J_{5,9a}$ = 1.0 Hz, $J_{8,9a}$ = 1.7 Hz and $J_{9,9a}$ = 5.0 Hz), 5.72 (br d, H-5, $J_{5,6}$ = 6.6 Hz), 5.87 (ddddd, H-9, $J_{5,9} = J_{6,9} = J_{7,9}$ = 0.7 Hz, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 5.0 Hz), 6.27 (br ddd, H-8, $J_{7,8}$ = 5.7 Hz, $J_{8,9}$ = 9.5 Hz and $J_{8,9a}$ = 1.7 Hz), 6.57 (br dd, H-7, $J_{6,7}$ = 11.0 Hz and $J_{7,8}$ = 5.7 Hz), 6.72 (br dd, H-6, $J_{5,6}$ = 6.6 Hz and $J_{6,7}$ = 11.0 Hz), 7.35-7.6 (aromatic protons)] some line broadening was observed and conversion **6l**$\rightleftharpoons$**8l** was fast enough to be easily evidenced through the spin saturation transfer effect. Irradiation of H-9a (H-5) of the "condensed" isomer (**8l**) led to a remarkable decrease (due to spin saturation transfer) in intensity of the signals both of H-5 (H-9a) of **8l** and of H-6 and H-11 of the "spiro" isomer (**6l**). Likewise, irradiation of H-6 and H-11 of **6l** brought about a

decrease in intensity of the signals of H-5 and H-9a of **8l** as expected for protons which convert into each other in an isomerization process taking place with a rate > 10^{-2} s^{-1}.[12] Taking advantage of the fact that the two forms (**6l**) and (**8l**) exhibited a similar population in CD_3CN, the exchange rate could be roughly evaluated as 1.42 s^{-1} (at 20 °C) by irradiating the methyl group of **8l** and measuring the intensity reduction [M(0)/M(∞) = 4.2] of the methyl group [relaxation time (T_1) = 2.45 s] of **6l**.[12] Line broadening of the ^1H nmr spectrum of **6l/8l** in *MeOD* at 20 °C was stronger than that in CD_3CN and signals sharpened only at ≤ 0 °C. These data provide clear evidence that an increase in solvent polarity is paralleled by an enhancement in equilibration rate between **6** and **8**.

The presence of two aryl residues at position 3 and 4 makes the rearrangement between **6** and **8** faster. Thus, in the case of **6e/8e** (R^1 = Ph; R^2 = *p*-MeC_6H_4) and of **6g/8g** (R^1 = *p*-$NO_2C_6H_4$; R^2 = *p*-MeC_6H_4) a sharp appearance for all ^1H nmr signals ($CDCl_3$) could be observed only at temperatures ≤ -10 °C and ≤-20 °C, respectively.

When the R^1 group is an efficient electron attracting group as in **6n/8n**, **6o/8o** and **6p/8p** (R^1 = MeCO, PhCO and COOEt, respectively; R^2 = *p*-MeC_6H_4), equilibration between the two isomers becomes so fast on the nmr time scale that the coalescence temperature is below room temperature. For example, the ^1H nmr spectrum of **6n/8n** (R^1 = MeCO; R^2 = *p*-MeC_6H_4) at 20 °C in $CDCl_3$ displayed two singlets at δ 2.32 (MeC_6H_4) and 2.44 (MeCO), a very broad singlet at δ 5.45 (2 H, H-6 and H-11 of **6n** and H-5 and H-9a of **8n**), two complex multiplets at δ 6.32 and 6.39 (each representing two protons, H-7, H-8, H-9 and H-10 of **6n** and *H-6, H-7, H-8* and H-9 of **8n**) and two multiplets at δ 6.89 and 7.11 (AA'XX' system, *p*-MeC_6H_4). At 50 °C an almost averaged spectrum was observed as shown by the fact that the broad singlet at δ 5.45 was split into a broad doublet (J = 9.0 Hz) while line sharpening was observed for the other signals. To freeze the system (on the nmr time scale) we had to go down to -70 °C [**6n/8n** = 80:20; **6n**: ^1H Nmr δ (ppm, CD_2Cl_2) 2.33 (s, *p*-MeC_6H_4), 2.56 (s, MeCO), 5.98 (bd, H-6 and H-11, J = 11.0 Hz), 6.54 (m, H-7 and H-10), 6.63 (m, H-8 and H-9), 6.91 and 7.15 (two m, 4 H, AAXX' system of the *p*-tolyl group); ^{13}C nmr δ (ppm, CD_2Cl_2) 20.3 (Me), 27.6 Me), 100.6 (C-5), 125.1, 126.2, 127.4, 128.9 and 129.6 (aromatic and vinyl CH), 133.8 and 135.8 (quaternary aromatic carbons), 150.3 (C-3), 188.2 (CO). **8n**: ^1H Nmr δ (ppm, CD_2Cl_2) 2.40 and 2.45 (two s, MeCO and *p*-MeC_6H_4), 3.78 (br d, H-9a, $J_{9,9a}$ = 5.2 Hz), 5.33 (br d, H-5, $J_{5,6}$ = 5.6 Hz), 5.96 (br dd, H-9, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 5.2 Hz), 6.39 (m, H-8, $J_{7,8}$ = 5.0 Hz and $J_{8,9}$ = 9.5 Hz), ≈ 6.6 (H-6 and H-7 buried under the signals of **6n**), 7.28 (br d, 2 H, aromatic protons; the other two are buried under signals of **6n**); ^{13}C nmr δ (ppm, CD_2Cl_2) 20.5 (Me), 27.8 (Me), 73.1 (C-9a), 100.7 (C-5), 122.8, 124.8, 126.8, 128.5 and 129.3



6 **7** **8**

(aromatic and vinyl CH), 134.6 and 137.9 (quaternary aromatic carbons), 145.8 (C-3), 191.6 (CO)]. All the above data provide compelling evidence in favor of an easy rearrangement process between **6** and **8** which takes place *via* zwitterion (**7**). In this intermediate charges are stabilized by delocalization and held close to each other to lessen the electrostatic work necessary to separate them. Thus, formation of **7** is energetically little expensive.

We now discuss factors that control the **6/8** ratios. These ratios are solvent (see Table 1) and temperature dependent. For example, the **6j/8j** ratio was found to be 10:90, 25:75, 38:72 and 47:53 in deuterobenzene, deuterotoluene, deuterochloroform and deuteroacetonitrile, respectively, at 20 °C while at 60 °C in deuterotoluene it changed to 40:60. In the case of the **6l/8l** mixture the ratios were as follows: 30:70, 29:71 and 44:56 in deuterobenzene, deuterochloroform and deuteroacetonitrile, respectively, at 20 °C and 53:47 in deuteroacetonitrile at 40 °C. In deuterotoluene the **6l/8l** ratio changed from 13:87 at -10 °C to 31:69 at +40 °C. A reversal of the **6k/8k** ratio was observed on passing from deuterobenzene (30:70) to deuteroacetonitrile (58:42) at 20 °C. In short, a temperature increase favored **6** over **8** and on going from deuterobenzene (or deuterotoluene and deuterochloroform) to deuteroacetonitrile there always was a significant increase in the **6/8** ratio (the more polar solvent adds a favor 0.3-1.2 kcal mol^{-1} to the "spiro" over the "condensed" isomer) suggesting a higher dipole moment for **6** as compared to **8**.

Inspection of Table 1 shows that **6/8** ratios are also heavily dependent on substituents R^1 and R^2. The *t*-butyl group at position 3 seems to be very efficient in shifting the equilibrium to the side of **6** (**6a/8a** and **6b/8b** >20 in C_6D_6 and CD_3CN), whereas the opposite, although to a lesser extent, is true for the Me group both at 3 and 4 positions (Entries **j-m**, **6/8** ≤0.7 in C_6D_6 and ≤ 1.4 in CD_3CN). Particularly striking is the complete reversal of the equilibrium ratio upon replacing the bulky *t*-Bu group (R^1 = *t*-Bu, R^2 = Me; **6a/8a** >20) at position 3 by another bulky group, i.e. the *o*,*o*'-dichlorophenyl group (R^1 = 2,6-$Cl_2C_6H_3$, R^2 = Me; **6m/8m** = 0.06). This finding cannot be explained as a result of a change in the electronic characteristic of the substituent. In fact, introduction of either electron donating or electron attracting groups in para position of a phenyl residue, located at 3 and 4 position of **6** and **8** (Entries **c-g**, **6/8** = 95:5 - 90:10), did not give rise to a strong effect on the isomer ratio suggesting that electronic effects of substituents, which are so important in determining the equilibration rate, do not play a relevant role in determining the equilibrium ratios. When the substituent was introduced in ortho position (i.e., R^1 = *o*-$NO_2C_6H_4$; R^2 = *p*-MeC_6H_4; **6i/8i** = <20:80, Table 1) a clear-cut reversal of the **6/8** ratio was observed and the "condensed" isomer became strongly dominant, *i.e.*, an ortho substituted phenyl group at position 3 highly favors the "condensed" form.

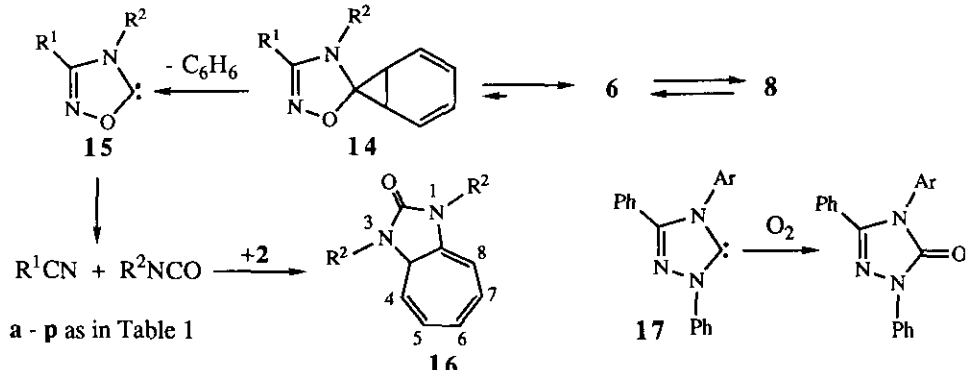
Preliminary result of semiempirical MO calculations[13] on the relative stability of **6** and **8** indicate that these calculations are not able to satisfactorily reproduce the experimental data. We will refer on these data in due course but for now we are left with qualitative reasonings. We feel that the equilibrium ratios between **6** and **8** are the result of a subtle interplay of steric interactions. The different effect of the *t*-Bu group vs ortho substituted phenyl groups is, probably, simply a reflection of the fact that these latters can minimize steric interactions through conformational isomerism whereas this is not a possibility for the symmetric *t*-Bu group.[14] The above

data also suggest that the relative intrinsic energies of the parent compounds (**6**) and (**8**) ($R^1 = R^2 = H$) should lie within a few kcal mol^{-1}, but they do not allow to establish which one of the two isomers is more stable. Moreover, we can safely attribute to a lessening of steric interactions the complete shift toward the "condensed" forms (**C**) and (**D**) of the equilibrium involving the adducts of diphenylnitrile imine to **2** (*Scheme* 2).[4]

As far as we know the **6** ⇌ **8** equilibrium provides the first example of a fast reversible equilibrium between a 7,7-disubstitutedcycloheptatriene and a 1,7-disubstitutedcycloheptatriene in which both forms are present in significant amounts.[15]

REACTIONS OF COMPOUNDS (6/8)

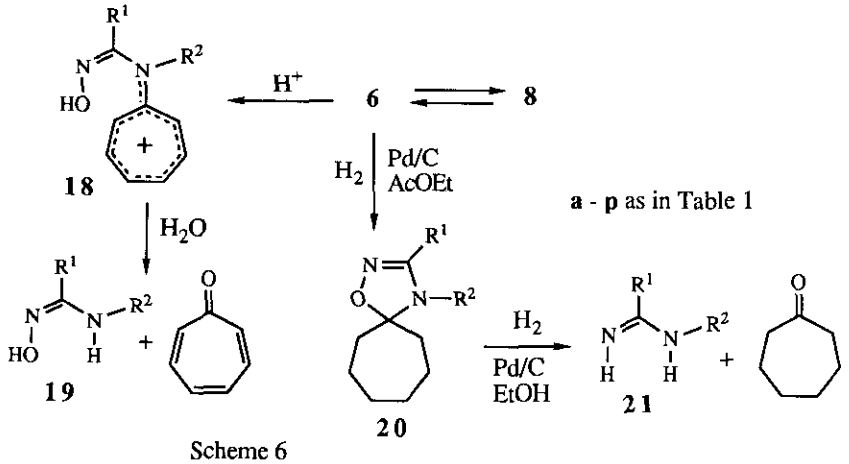
Compounds (**6/8**) decomposed to benzene, R^1CN and R^2NCO upon heating (Scheme 5). For example, the nitrile and the isocyanate were the only products detected when mixtures (**6/8**) were analyzed by gc (injector at 250 °C). However, this decomposition also took place under much milder conditions. Thus, good yields of benzonitrile and *p*-tolyl isocyanate were obtained by heating **6e/8e** (R^1 = Ph; $R^2 = p$-MeC_6H_4) in an apparatus for sublimation at 120 °C and high yields of *p*-tolyl urea were isolated by heating the same compound in refluxing toluene in the presence of *p*-toluidine. Moreover, the signal of benzene appeared in the ^1H nmr spectra of **6/8** (not only in the case of compounds in which the "spiro" form was dominant as for **6e/8e** but also for those, i.e. **6/8j**, **k** and **l**, in which the "condensed" form was prevalent) when solutions of these compounds in C_7D_8, $CDCl_3$ and CD_3CN were heated above 40 °C. A surprisingly fast decomposition was observed in the case of **6a** (R^1 = *t*-Bu; R^2 = Me) and **6b** (R^1 = *t*-Bu; $R^2 = p$-MeC_6H_4). Monitoring of a $CDCl_3$ solution of **6a** and **6b** by ^1H nmr showed that these compounds decomposed smoothly at room temperature (≈ 20 °C; **6a**: 75% conversion after 5 days; **6b**: 33% conversion after 3 days). Moreover, in the reaction of **1b** (slowly generated in situ with sodium bicarbonate) with **2b** in benzene at room temperature we isolated, aside from **6b**, substantial amounts (15%) of the adduct of *p*-tolyl isocyanate with azaheptafulvene (**2b**), *i.e.* **16** ($R^2 = p$-MeC_6H_4) (Scheme 5).



Scheme 5

The most straightforward way to explain decomposition of **6/8** is to assume that the "spiro" isomer (**6**) is in equilibrium with a very small (undetectable by nmr) quantity of the "norcaradiene" isomer (**14**) which enters a facile cheletropic fragmentation to give benzene and the heterocyclic carbene (**15**). This latter, in turn, decomposes to R^1CN and R^2NCO. On the basis of the behavior of **6a** and **6b** and of the observation that under similar conditions **6m/8m** (8:92 in $CDCl_3$) did not decompose appreciably, one can suggest that decomposition is more facile for compounds in which the "spiro" form is dominant, as in the case of **6a** and **6b**. However, the higher fragmentation rate of **6k/8k** [11% conversion after 6 days in $CDCl_3$ (**6k/8k** = 35:65) at 20 °C] as compared to that of **6g/8g** (**6g/8g** ≈ 90:10, 1-2% conversion, under the same conditions of **6k/8k**) demonstrates that other factors (*e.g.*, substituents might heavily influence the equilibrium **6**⇌**14** as well as the fragmentation rate of **14**) play a role. The fragmentation of **15** is much more facile than that of **17**, which survives long enough to react with atmospheric oxygen.[4]

Hydrolysis under acidic conditions (acetic acid) of **6/8** afforded tropone and amidoxime (**19**) most probably *via*



Scheme 6

the tropylium ion (**18**) (Scheme 6).

The "spiro" form (**6**) reacted more readily than the "condensed" form (**8**) with hydrogen in the presence of Pd/C and, as a consequence of the fast interconversion between the two isomers, only products derived from the "spiro" form were obtained. In fact, we managed to hydrogenate selectively the cycloheptatriene moiety of **6** to give good yields of **20** with Pd/C in ethyl acetate while in ethanol also the heterocyclic ring was easily cleaved to give amidine (**21**) and cycloheptanone (Scheme 6).

Further studies dealing with the Diels-Alder reactions of **6/8** with N-methyltriazolinedione and tetracyanoethene are in progress in our laboratory. Preliminary results indicate that adducts derived (at least formally) from the "condensed" form are formed in these reactions.

EXPERIMENTAL

Melting points are uncorrected and were measured with a Büchi 535 apparatus. Adducts (**6/8**) tend to decompose upon heating. Consequently, the melting point is not a reliable physical datum to characterize these compounds being it highly dependent on how fast the melting point is reached. Elemental analyses were made on a Carlo Erba CHN analyser, model 1106. Infrared spectra were recorded as either Nujol suspensions or films on a Perkin-Elmer 881 spectrophotometer. ^1H And ^{13}C nmr spectra were recorded on a Bruker AE 300 (operating at 300.3 and 75.5 MHz, respectively) spectrometer with tetramethylsilane as internal standard at 20 °C (unless otherwise stated) for $CDCl_3$, C_6D_6, C_7D_8 and CD_3CN solutions. Protons were correlated by decoupling experiments. Assignments were secured by $^1H/^{13}C$ heterocorrelated spectra. ^1H Nmr spectra were evaluated as first order spectra. The ^1H nmr spectra in CD_3CN were very similar to those in $CDCl_3$ while in C_6D_6 (and in C_7D_8) chemical shifts (both absolute and relative values) were different. However, the diagnostic features of these spectra are independent of the solvent used. In the case of compounds (**6**) the olefinic protons (H-6, H-7, H-8 and H-11) constitute a complex AA'BB'CC' system. Only the largest separation of the multiplet corresponding to H-6 and H-11 will be reported. Gc analyses were carried out with a DANI 6500, PTV injector, CP-Sil-19CB (25 m) capillary column and carrier H_2. Thin-layer chromatograms were done on plates precoated with silicagel 60 GF_{254} (Merck). Spots were visualized either by spraying with 3% chromic oxide in sulphuric acid (50%) followed by heating at 120 °C or under uv light. Column chromatography was performed with silica gel 60 (70-230 mesh) Merck eluting with cyclohexane/ethyl acetate, benzene and benzene/ethyl acetate mixtures. Hydroximic acid chlorides[16] and azaheptafulvenes (**2**)[7,17] were prepared according to literature procedures.

***Reactions of nitrile oxides* (1) *with azaheptafulvenes* (2).** The nitrile oxides (**1a-k**) were generated in situ from the corresponding hydroximic acid chlorides. Thus, a solution of the hydroximic acid chloride (1.1 mmol) in benzene (10 ml) and a solution of triethylamine (112 mg, 1.1 mmol) in benzene (10 ml) were added at the same time to a solution of azaheptafulvene (**2**) (1.00 mmol) and triethylamine (15 mg, 0.15 mmol) in benzene (10 ml) dropwise (2-3 h) under stirring at room temperature. The reaction mixture was left aside for further 3-9 h, washed with water to remove triethylamine hydrochloride and dried with anhydrous sodium sulfate. Tlc analysis of the crude reaction product showed the presence of only one spot for the adducts aside from that of the nitrile oxide dimer. After evaporation of the solvent under reduced pressure at room temperature the pure adduct was isolated in high yields either by a fast crystallization or by column chromatography. Unidentified products, when detected, were present in small amounts. In an alternative methodology the nitrile oxide was slowly generated *in situ* from the hydroximic acid chloride with excess solid sodium bicarbonate under otherwise similar conditions to give very similar results to those obtained by using triethylamine. However, the longer reaction times required by this latter method to reach 100% conversion from hydroximic acid chloride to nitrile oxide (*e.g.*, ≈ 4 h , ≈ 24 h and ≈ 48 h in the case of **1e**, **1g** and **1b**, respectively) might lead to some decomposition of the adduct. The yields reported below are for reactions in which triethylamine was used as base.

6a (60%), slight yellow platelets from petrol ether, mp 80-81 °C (Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.5; H, 8.3; N, 12.8. Found: C, 71.6; H, 8.4; N, 12.6.). ^{1}H Nmr δ (ppm, $CDCl_3$) 1.28 (s, Me_3C), 2.58 (s, Me), 5.81 (m, 2 H, H-6 and H-11, J = 11.0 Hz), 6.41 (m, 4 H, H-7, H-8, H-9 and H-10); δ (ppm, C_6D_6) 1.12 (s, Me_3C), 2.19 (s, Me), 5.83 (m, 2 H, H-6 and H-11, J = 11.0 Hz), 5.99 (m, 4 H, H-7, H-8, H-9 and H-10); ^{13}C nmr δ (ppm, C_6D_6) 28.2 (q, $\underline{Me}_3C$), 29.0 (q, MeN), 31.7 (s, $Me_3\underline{C}$), 99.7 (s, C-5), 126.7 (d, C-7 and C-10), 127.4 (d, C-6 and C-11), 129.5 (d, C-8 and C-9), 159.4 (s, C-3).

6b (65%), colorless needles from petrol ether, mp 62-64 °C (Anal. Calcd for $C_{19}H_{22}N_2O$: C,77.5; ; H, 7.5; N, 9.5. Found: C, 77.7; H, 7.4; N, 9.3). When **1b** was generated with sodium bicarbonate as base in the presence of **2b** (reaction time >48 h) also compound **16** [R^2 = p-MeC_6H_4; 15% , colorless crystals from benzene/petrol ether, mp 166-167 °C; ir (ν, cm^{-1}) 1723 (s) and 1624 (s); ^{1}H nmr δ (ppm, $CDCl_3$) 2.33 (s, Me), 2.39 (s, Me), 4.46 (m, H-3a), 5.02 (br dd, H-4, $J_{3a,4}$ = 3.5 Hz and $J_{4,5}$ = 8.7 Hz), 5.56 (br dd, H-8, $J_{3a,8}$ = 2.2 Hz and $J_{7,8}$ = 6.7 Hz), 6.22 (br ddd, H-5, $J_{3a,5}$ = 1.8 Hz, $J_{4,5}$ = 8.7 Hz and $J_{5,6}$ = 5.8 Hz), 6.37 (dddd, H-6, $J_{4,6} \approx J_{6,8}$ = 0.7 Hz, $J_{5,6}$ = 5.8 Hz and $J_{6,7}$ = 11.1 Hz), 6.53 (br dd, H-7, $J_{6,7}$ = 11.1 Hz and $J_{7,8}$ = 6.7 Hz), 7.21 and 7.55 (AA'XX' system, *p*-$MeC_6\underline{H}_4$), 7.28 (s, 4 H, *p*-$MeC_6\underline{H}_4$); ^{13}C nmr δ (ppm, $CDCl_3$) 20.6 (Me), 21.0 (Me), 56.7 (C-3a), 95.3 (C-8), 116.2, 123.9, 125.4 and 129.2 (C-4 - C-7), 116.8, 126.7, 129.5 and 129.9 (aromatic CH), 131.7, 133.0, 133.6, 135.0 and 137.6 (C-8a and quaternary aromatic carbons), 154.2 (CO)], aside from **6b** (60%), was isolated. Compound (**16**) was identical to the reaction product of p-tolyl isocyanate with **2b**.

6c/8c (90%), yellow prisms from methanol, mp 109-110 °C decomp. (lit., 91-92 °C)[6] (Anal. Calcd for $C_{20}H_{15}N_2OCl$: C, 71.6; H, 4.5; N, 8.4. Found: C, 71.3; H, 4.6; N, 8.5.). **6c**: ^{1}H Nmr δ (ppm, C_6D_6) 5.92 (m, 6 H, H-6 - H-11), 6.50 and 6.74 (AA'XX' system, *p*-$MeC_6\underline{H}_4$), 6.93 and 7.52 (AA'XX' system, *p*-ClC_6H_4). **8c**: ^{1}H Nmr δ (ppm, C_6D_6) 4.11(br d, H-9a, $J_{9,9a}$ = 5.0 Hz), 5.17 (m, H-5).

6d/8d (92%), colorless prisms from methanol, mp 110-111 °C decomp. (lit., 118-119 °C)[6] (Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.3; H, 5.5; N 8.5. Found: C, 76.4; H, 5.4; N, 8.5.). **6d**: ^{1}H Nmr δ (ppm, C_6D_6) 3.12 (s, MeO), 6.02 (br s, 6 H, H-6 - H-11), 6.41 and 6.93 (AA'XX' system, *p*-$MeOC_6\underline{H}_4$), 6.73 and 7.68 (two m, 3 H and 2 H, Ph). **8d**: ^{1}H Nmr δ (ppm, C_6D_6) 3.02 (s, MeO), 4.19 (br d, H-9a, $J_{9,9a}$ = 5.0 Hz), 5.36 (m, H-5).

6e/8e (91%), slightly yellow prisms from methanol, mp 100-101 °C decomp. (lit., 92-94 °C)[6] (Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.2; H, 5.8; N, 8.5. Found: C, 80.2; H, 5.7; N, 8.6.). **6e**: ^{1}H Nmr δ (ppm, $CDCl_3$ at - 20 °C) 2.25 (s, Me), 6.05 (br d, H-6 and H-11, J = 10.5 Hz), 6.52 (m, 4 H, H-7 - H-10), 6.77 and 6.98 (AA'XX' system, *p*-$MeC_6\underline{H}_4$), 7.28, 7.36 and 7.46 (three m, 2 H, 1 H and 2 H, Ph); ^{13}C nmr δ (ppm, $CDCl_3$) 20.7 (q, Me), 99.4 (s, C-5), 127.2 (d, C-7 and C-10), 127.3 (d, C-6 and C-11), 129.6 (d, C-8 and C-9), 126.8, 128.0, 128.2, 129.2 and 129.9 (aromatic CH), 125.7, 135.4 and 135.5 (quaternary aromatic carbons), 153.5 (C-3). **8e**: ^{1}H Nmr δ (ppm, $CDCl_3$ at - 20 °C) ≈ 2.25 (Me), 3.80 (br dd, H-9a, $J_{9,9a}$ = 5.4 Hz and J = 1.0 Hz), 5.39 (br d, H-5, $J_{5,6}$ = 5.5 Hz), 6.17 (br dd, H-9, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 5.4 Hz), 6.47 (m, H-8, $J_{7,8}$ = 5.0 Hz), ≈ 6.52 (H-6 and H-7, buried under signals of **6e**); ^{13}C nmr δ (ppm, $CDCl_3$) 73.7 (C-9a) and 100.5 (C-5).

6f/8f (85%), slightly yellow needles from methanol, mp 135 °C decomp. (lit., 131-132 °C)[6] (Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.7; H, 5.9; N, 8.1. Found: C, 76.5; H, 6.1; N, 8.3.). **6f**: ^{1}H Nmr δ (ppm, C_6D_6) 1.92 (s, MeC), 3.10 (s, MeO), 6.05 (m, 6 H, H-6 - H-11), 6.52 and 7.61 (AA'XX' system, *p*-$MeOC_6\underline{H}_4$), 6.69 and

6.79 (AA'XX' system, *p*-MeC$_6$H$_4$). **8f**: ^{1}H Nmr δ (ppm, C$_6$D$_6$) 1.81 (s, MeC), 3.02 (s, MeO), 4.20 (br d, H-9a, $J_{9,9a}$ = 5.0 Hz), 5.40 (m, H-5).

6g/8g (88%), slightly yellow needles from methanol, mp 128 °C decomp. (Anal. Calcd for $C_{21}H_{17}N_3O_3$: C, 70.2; H, 4.8; N, 11.7. Found: C, 70.3; H, 4.8; N, 11.7.). **6g**: ^{1}H Nmr δ (ppm, $CDCl_3$ at - 20 °C) 2.29 (s, Me), 6.03 (br d, H-6 and H-11, J = 10.5 Hz), 6.55 (m, 4 H, H-7 - H-10), 6.78 and 7.02 (AA'XX' system, *p*-MeC$_6$H$_4$), 7.67 and 8.18 (AA'XX' system, *p*-NO$_2$C$_6$H$_4$). **8g**: ^{1}H Nmr δ (ppm, $CDCl_3$ at - 20 °C) ≈ 2.29 (Me), 3.87 (dd, H-9a, $J_{9,9a}$ = 5.0 Hz and J = 1.0 Hz), 5.96 (br d, H-5, $J_{5,6}$ = 5.8 Hz), 6.13 (br dd, H-9, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 5.0 Hz), 6.39 (m, H-8, $J_{7,8}$ = 5.5 Hz), ≈ 6.52 (H-6 and H-7, buried under the signals of **6g**), 6.98 and 7.09 (AA'XX' system, *p*-MeC$_6$H$_4$), 7.47 and 8.06 (AA'XX' system, *p*-NO$_2$C$_6$H$_4$).

6h/8h (86%), slightly yellow needles from methanol, mp 131 °C decomp. (Anal. Calcd for $C_{21}H_{17}N_3O_3$: C, 70.2; H, 4.8; N, 11.7. Found: C, 70.0; H, 4.7; N, 11.9.). **6h**: ^{1}H Nmr δ (ppm, $CDCl_3$ at - 10 °C) 2.25 (s, Me), 6.02 (br d, H-6 and H-11, J = 10.5 Hz), 6.51 (m, 4 H, H-7 - H-10), 6.78 and 7.01 (AA'XX' system, *p*-MeC$_6$H$_4$), 7.50, 7.70, 8.22 and 8.33 (t, br d, br d and br s, m-NO$_2$C$_6$H$_4$). **8h**: ^{1}H Nmr δ (ppm, $CDCl_3$ at - 10 °C) ≈ 2.25 (Me), 3.86 (br dd, H-9a, $J_{9,9a}$ = 5.1 Hz and J = 1.0 Hz), 5.92 (br d, H-5, $J_{5,6}$ = 5.8 Hz), 6.12 (br dd, H-9, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 5.1 Hz), 6.38 (m, H-8, $J_{7,8}$ = 5.8 Hz), ≈6.51 (H-6 and H-7), 7.02 and 7.08 (AA'XX' system, *p*-MeC$_6$H$_4$), 7.39, 7.62, 8.09 and 8.11(t, br d, br d and br s, *m*-NO$_2$C$_6$H$_4$).

6i/8i (70%), yellow viscous oil purified by chromatography (Anal. Calcd for $C_{21}H_{17}N_3O_3$: C, 70.2; H, 4.8; N, 11.7. Found: C, 70.6; H, 4.6; N, 11.8.). **6i**: ^{1}H Nmr δ (ppm, CD_3CN at - 30 °C) 6.14 (m, 2 H, H-6 and H-11), 6.53 (m, 4 H, H-7 - H-10). **8i**: ^{1}H Nmr δ (ppm, CD_3CN at - 30 °C) 3.62 (br dd, H-9a, $J_{9,9a}$ = 5.5 Hz and J = 1.0 Hz), 5.18 (br d, H-5, $J_{5,6}$ = 6.0 Hz), 6.08 (br dd, H-9, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 5.5 Hz), 6.39 (m, H-8, $J_{7,8}$ = 5.5 Hz), 6.62 (m, H-6 and H-7). In this ^{1}H nmr spectrum there are two other lower intensity signals [δ 3.89 (br d, H-9a, $J_{9,9a}$ = 5.0 Hz) and δ 5.15 (m, H-5)] also attributable to a "condensed" form which suggest that actually the "condensed" isomer (**8i**) is a mixture of two conformers converting into each other slowly on the nmr time scale at -30 °C (ratio between conformers of **8i** = 3:1; ratio **6i/8i** (both conformers of **8i**) = 35:65). The ^{1}H nmr spectrum of the mixture (**6i/8i**) in C_7D_8 at -40 °C exhibited a further complication: signals attributable to three conformers (A/B/C = 11:1.6:1.0) of **8i** were present [A: δ 3.91 (dd, H-9a, $J_{9,9a}$ = 5.5 Hz and $J_{8,9a}$ ≈ 1.0 Hz) and 5.21 (br d, H-5, $J_{5,6}$ = 5.8 Hz); B: δ 4.48 (br d, H-9a, $J_{9,9a}$ = 4.9 Hz) and 5.11 (br d, H-5, $J_{5,6}$ ≈ 6.5 Hz); C: 3.89 (m, H-9a) and 5.14 (br d, H-5, $J_{5,6}$ = 5.5 Hz)]. Overlapping of signals prevented a precise evaluation of the **6i/8i** ratio both in C_6D_6 and in C_7D_8.

6j/8j (50%), slight yellow prisms from petrol ether, mp 58-61 °C (Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.2; H, 6.9; N 15.9. Found: C, 68.4; H, 7.0; N, 16.0 .).

6k/8k (80%), slight yellow prisms from petrol ether, mp 82-83 °C (Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.2; H, 6.4; N, 11.1. Found: C, 76.5; H, 6.2; N, 11.3.). **6k**: ^{1}H Nmr δ (ppm, C$_6$D$_6$) 1.57 (s, Me), 1.99 (s, Me), 5.86 (m, H-8 and H-9), 5.97 (m, H-7 and H-10), 6.03 (m, H-6 and H-11), 6.68 and 6.75 (AA'XX' system, *p*-MeC$_6$H$_4$); ^{13}C nmr δ (ppm, $CDCl_3$) 9.8 (q, Me), 20.8 (q, Me), 97.8 (s, C-5), 124.5 (d, C-7 and C-10 or C-8 and C-9), 126.9 (d, C-6 and C-11), 129.2 (d, C-8 and C-9 or C-7 and C-10), 128.1, 129.4, 133.4 and 136.9 (d, d, s and s, *p*-MeC$_6$H$_4$), 150.7 (s, C-3). **8k**: ^{1}H Nmr δ (ppm, C$_6$D$_6$) 1.56 (s, Me), 1.98 (s, Me), 3.96 (ddd,

H-9a, $J_{5,9a}$ = 1.0 Hz, $J_{8,9a}$ = 1.2 Hz and $J_{9,9a}$ = 4.8 Hz), 5.00 (m, H-5), 6.12 (m, H-8), 6.23 (ddddd, H-9, $J_{5,9}$ =$J_{6,9}$ = $J_{7,9}$ = 0.6 Hz, $J_{8,9}$ = 9.5 Hz and $J_{9,9a}$ = 4.8 Hz), 6.31 (m, H-6 and H-7; the coincidence of the chemical shifts of these two protons gave rise to strong second order effects on the signals of H-5 and H-8), 6.53 and 6.74 (AA'XX' system, *p*-Me$C_6\underline{H}_4$); ^{13}C nmr δ (ppm, $CDCl_3$) 18.1 (q, Me), 21.0 (q, Me), 72.6 (d, C-9a), 99.6 (d, C-5), 122.5(d, C-9), 126.9 (d, C-8), 126.5 and 128.8(two d, C-6 and C-7), 129.5 (s, C-4a), 128.5, 130.4, 135.5 and 138.8 (d, d, s and s, *p*-Me$\underline{C}_6H_4$), 149.4 (s, C-3). Aside from **6k/8k** we isolated a yellow-orange adduct (i.e., **4k/5k**, ≈ 3%, viscous oil) with higher R_f than **6k/8k** which we did not manage to freed from minor impurities. When the reaction was carried out in methanol (by using solid sodium bicarbonate as base, 4 h at room temperature) the spot of **4k/5k** could not be detected by tlc analysis of the crude reaction mixture while compounds (**6k/8k**) were isolated in 75% yields by column chromatography.

6l/8l (55%), colorless prisms from methanol, mp 101-103 °C (Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.6; H, 5.9; N, 11.8. Found: C, 75.5; H, 5.9; N, 11.6.).

6m/8m (75%), colorless needles from cyclohexane, mp 102-103 °C decomp.(Anal. Calcd for $C_{15}H_{12}N_2OCl_2$: C, 58.6; H, 3.9; N 9.1. Found: C, 58.9; H, 3.9; N, 9.0.).

6n/8n (76%), slight yellow prisms from methanol, mp 95-97 °C (Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.8; H, 5.8; N, 10.0. Found: C, 72.8; H, 5.6; N, 10.1.).

6o/8o (75%), yellow oil purified by chromatography (Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.2; H, 5.3; N, 8.2. Found: C, 77.4; H, 5.5; N, 8.2.). **6o**: ^{1}H Nmr δ (ppm, CD_2Cl_2 at - 50 °C) 2.28 (s, Me), 6.08 (br d, H-6 and H-11, J = 10.5 Hz), 6.58 (m, 4 H, H-7 - H-10), 6.98 and 7.16 (AA'XX' system, *p*-Me$C_6\underline{H}_4$), 7.54, 7.72 and 8.19 (three m, 3 H, 1 H and 2 H, Ph). **8o**: ^{1}H Nmr δ (ppm, CD_2Cl_2 at - 50 °C) 2.28 (s, Me), 3.83 (br dd, H-9a, $J_{9,9a}$ = 5.3 Hz and J = 1.1 Hz), 5.39 (br d, H-5, $J_{5,6}$ = 5.9 Hz), 6.06 (br dd, H-9, $J_{8,9}$ = 9.6 Hz and $J_{9,9a}$ = 5.3 Hz), 6.40 (m, H-8, $J_{7,8}$ = 5.0 Hz), ≈ 6.58 (H-6 and H-7, buried under the signals of **6o**), 7.07 (m, 4 H, *p*-Me$C_6\underline{H}_4$), 7.49, 7.67 and 7.94 (three m, 3 H, 1 H and 2 H, Ph).

6p/8p (78%), yellow oil purified by chromatography (Anal. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.7; H, 5.9; N, 9.0. Found: C, 69.7; H, 5.9; N, 9.2.). **6p**: ^{1}H Nmr δ (ppm, CD_2Cl_2 at - 50 °C) 6.00 (br d, H-6 and H-11, J = 10.0 Hz), 6.57 (m, 4 H, H-7 - H-10). **8p**: ^{1}H Nmr δ (ppm, CD_2Cl_2 at - 50 °C) 3.79 (br dd, H-9a, $J_{9,9a}$ = 5.3 Hz and J = 1.1 Hz), 5.39 (br d, H-5, $J_{5,6}$ = 5.8 Hz), 5.98 (br dd, H-9, $J_{8,9}$ = 9.6 Hz and $J_{9,9a}$ = 5.3 Hz), 6.38 (m, H-8, $J_{7,8}$ = 5.0 Hz), ≈ 6.58 (H-6 and H-7, buried under the signals of **6p**); the ^{1}H nmr spectrum also displayed three pairs of signals (the signals of each pair exhibited the same intensity), i.e., two triplets at δ 1.05 and 1.29 ($J_{CH2,Me}$ = 7.5 Hz), two singlets at δ 2.33 and 2.39 and two quartets at δ 4.02 and 4.28. Aromatic protons absorbed at δ 6.95 and 7.19 and at δ 7.15 and 7.29.

Competition reactions were carried out by generating benzonitrile oxide from benzohydroximic acid chloride (0.35 mmol) with triethylamine in the presence of an excess mixture of **2c** (0.5 mmol) and *N*-phenylmaleimide (0.5 mmol in benzene and 0.75 mmol in MeCN) during 2 h at 21 °C in benzene and acetonitrile, respectively, as described above. After further 3 h the solution was washed with water, dried with anhydrous sodium sulfate and evaporated. From adduct ratios (evaluated by ^{1}H nmr, two runs) k(**2c**): k(NPM) = 0.80 in benzene and = 3.5 in acetonitrile was evaluated.[18]

Thermal decomposition of compounds (6/8). Compound (**6e/8e**) (1.10 mmol) was heated in an apparatus for sublimation at 120 °C under reduced pressure (≈ 30 mm Hg). The sublimed colorless oil (70%) consisted of a mixture of benzonitrile and *p*-tolyl isocyanate (ir). This oil was dissolved in benzene and treated with p-toluidine to give bis(*p*-tolyl)urea (mp 261-263 °C) (64%) identical in all respects to an authentic sample. Bis(*p*-tolyl)urea was also obtained by heating **6e/8e** in refluxing toluene (88%) and **6k/8k** in refluxing benzene (78%) in the presence of *p*-toluidine. Bis(*p*-tolyl)urea was also formed when adducts (**6/8**) (R^2 = p-MeC_6H_4) were heated during the work-up and a bitter-almond odor (benzonitrile) developed when compounds (**6/8**) (R^1 = Ph) were heated at the melting point or in solution. Benzene could be easily detected (singlet at ≈ δ 7.37 in $CDCl_3$ and CD_3CN and at ≈ δ 7.12 in C_7D_8) when decomposition of **6/8** was carried out in deuterated solvents and followed by ^1H nmr. Decomposition of **6c/8c** and **6h/8h**, respectively, was performed either at 60 °C in C_7D_8 for 50 h or in $CDCl_3$ at 40 °C for 5 days. After that time the starting compound was still present in the reaction mixture but the signal of benzene and signals attributable to **11c** [i.e., δ 2.48 (t, 2 H, J = 6.8 Hz), 5.38 (dt, 1 H, J = 6.8 and 9.8 Hz), 5.48 (dt, 1 H, J = 6.8 and 9.8 Hz), 6.17 (d, 1 H, J = 9.8 Hz] and **11h**, respectively, were also present in the ^1H nmr spectrum. Compounds (**6/8**) were stable for months when kept at ≤ 0 °C in the dark.

Hydrolysis of compounds (6/8) under acidic conditions. Compounds (**6/8**) (0.5-0.9 mmol) were dissolved in acetic acid and left aside at room temperature. The yellow color of the solution faded with time. When 100% conversion was reached, as judged by tlc, the reaction mixture was poured cautiously in a solution of sodium bicarbonate (10% in water) and then extracted several times with diethyl ether. Tlc analysis showed the presence of tropone and of amidoxime (**19**) as the only important products. Amidoximes could be isolated in high yields (≥ 70%) by column chromatography. They all gave correct elemental analyses, consistent nmr spectra and were identical in all respects to amidoximes synthesized from the appropriate nitrile oxide and amine.[19] Also tropone (although in lower yields) was isolated and characterized.

19c: colorless needles from benzene, mp 175-176 °C decomp.; ir (ν, cm^{-1}) 3410 (m), 3200 (very broad, s), 1650 (s) and 1600 (m). **19d**: colorless prisms from petrol ether, mp 159-160 °C; ir (ν, cm^{-1}) 3410 (m), 3080 (very broad, s), 1635 (s). **19e**: colorless needles from benzene, mp 156-157 °C; ir (ν, cm^{-1}) 3400 (w), 3390 (w), 3375 (w), 3060 (very broad, s), 1635 (s) and 1610 (s). **19l**: colorless needles from benzene/petrol ether, mp 149-150 °C; ir (ν, cm^{-1}) 3398 (m), 3100 (very broad, s), 1652 (s). **19o**: colorless needles from benzene/cyclohexane, mp 153-155 °C; ir (ν, cm^{-1}) 3395 (m), 3260 (broad, s), 1680 (s) and 1645 (s).

Catalytic hydrogenation of compounds (6/8). A solution of compounds (**6c/8c**) and (**6k/8k**), respectively, (0.80 mmol) in ethyl acetate (25 ml) was hydrogenated in the presence of Pd/C (10%, 40 mg) at room temperature and under atmospheric pressure. After the absorption of 3.1 mol equiv of hydrogen (3-4 h) the catalyst was filtered off, the solvent evaporated and the residue column chromatographed to give pure **20c** (85%) and **20k** (72%), respectively. Aside from small amounts of products exhibiting very low R_f (probably amidines **21**), no other products were detected by tlc. Similar results were obtained for **6d/8d** and **6e/8e**.

20c: colorless needles from petrol ether, mp 113 °C (Anal. Calcd for $C_{20}H_{21}N_2OCl$: C, 70.5; H, 6.2; N, 8.2. Found: C, 70.4; H, 6.0; N, 8.1.); ^1H nmr δ (ppm, $CDCl_3$) 1.52 (m, 4 H), 1.67 (m, 4 H), 1.88 (m, 2 H), 2.20 (m, 2 H), 6.91 and 7.20 (AA'XX' system, *p*-ClC_6H_4), 7.25, 7.30 and 7.41 (three m, 2 H, 1 H and 2 H, Ph).

20k: colorless needles from petrol ether, mp 81-82 °C (Anal. Calcd for $C_{16}H_{22}N_2O$: C, 74.4; H, 8.6; N, 10.8. Found: C, 74.1; H, 8.5; N, 10.6.); ^{1}H nmr δ (ppm, $CDCl_3$) 1.38 (m, 4 H), 1.59 (m, 4 H), 1.73 (s, Me), 1.80 (m, 2 H), 2.15 (m, 2 H), 2.38 (s, Me), 7.03 and 7.19 (AA'XX' system, *p*-MeC_6H_4); ^{13}C nmr δ (ppm, $CDCl_3$) 9.85 (q, Me), 20.9 (q, Me), 21.5, 29.0 and 38.5 (three t, C-6 - C-11), 103.0 (s, C-5), 129.3, 129.8, 133.9 and 137.7 (d, d, s and s, *p*-MeC_6H_4), 152.4 (C-3).

Hydrogenation of **6c/8c** and **6k/8k**, respectively, (0.60 mmol) was also carried out in ethanol (20 ml) under otherwise similar conditions. Hydrogen uptake was faster than in ethyl acetate and five and four mol equiv of hydrogen were absorbed, respectively. In the case of **6c/8c** the hydrochloride of N-phenylbenzamidine (**21e**.HCl, $R^1 = R^2 =$ Ph, mp 227-228 °C) was isolated in 87% yield as also the C-Cl bond was cleaved under these conditions. N-Phenylbenzamidine (**21e**) (mp 112-114 °C) was obtained from the hydrochloride by treatment with a solution of sodium carbonate. Cycloheptanone was characterized as its 2,4-dinitrophenylhydrazone. In the case of **6k/8k**, after usual work-up, the oily residue was treated with petrol ether to give amidine (**21k**) [61%; colorless platelets from cyclohexane, mp 103-105 °C (Anal. Calcd for $C_9H_{12}N_2$: C, 72.9; H, 8.2; N, 18.9. Found: C, 73.0; H, 8.3; N, 19.0); ir (ν, cm^{-1}) 3452 (m), 3310 (m), 3000 (very broad, s), 1650 (s), 1606 (s); ^{1}H nmr δ (ppm, $CDCl_3$) 2.03 (br s, Me), 2.32 (s, Me), 4.45 (very broad signal), 6.78 and 7.06 (AA'XX' system, p-MeC_6H_4)]. Similar results were obtained for **6d/8d** and **6e/8e**.

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9. MO calculations were performed by using MNDO, AM1 and PM3 models as implemented in the HYPERCHEM package of programs.
10. The global minimum for **2a** was found to be a "tub" structure [ΔH_f° = 55.96 (MNDO), 65.11 (AM1) and 61.45 (PM3) kcal mol^{-1}; μ = 2.1 (MNDO), 1.85 (AM1) and 1.85 (PM3) D; $\varepsilon_{HO,\pi}$ = -8.93 (c_1 = 0.12; c_N = 0.32; MNDO), -8.89 (c_1 = 0.16; c_N = 0.37; AM1) and -8.94 (c_1 = 0.21; c_N = 0.39; PM3) eV; $\varepsilon_{lone\ pair}$ = -10.40 (MNDO), -10.10 (AM1) and -9.84 (PM3) eV; q_N (net atomic charge at the nitrogen atom) = -0.29 (MNDO), -0.19 (AM1) and -0.12 (PM3)] that is more stable than the planar structure [ΔH_f° = 58.13 (MNDO), 68.24 (AM1) and 63.20 (PM3) kcal mol^{-1}; μ = 2.27 (MNDO), 2.20 (AM1) and 2.02 (PM3) D; $\varepsilon_{HO,\pi}$ = -8.70 (c_1 = 0.15; c_N = 0.42; MNDO), -8.54 (c_1 = 0.19; c_N = 0.46; AM1) and -8.52 (c_1 = 0.22; c_N = 0.49; PM3) eV; $\varepsilon_{lone\ pair}$ = -10.36 (MNDO), -10.09 (AM1) and -9.83 (PM3) eV; q_N = -0.31 (MNDO), -0.21 (AM1) and -0.15 (PM3)]. In reference 1f the reported FOs parameters are for the planar structures of tropone and N-methylazaheptafulvene. However, it should be emphasized that also in the case of tropone the more stable structure is the "tub" structure [by ≈ 0.3 (MNDO), 0.7 (AM1) and 1.6 kcal mol^{-1} (PM3)] and not the planar form.
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13. Geometry optimization by semiempirical MO calculations revealed that the cycloheptatriene moiety of both **6** and **8** adopts a "tub" structure. Two minima were found in the case of **6** corresponding to conformers with the oxygen atom of the heterocyclic ring inside (**6I**) and outside (**6O**) the "tub", respectively. Only one minimum, with the oxygen atom outside, was found for **8**. As for comparison between the experimental data and the theoretical predictions, PM3 model, which gives the best results, correctly predicts dominance of **8j** (ΔH_f° = 62.06 kcal mol^{-1}; μ = 3.48 D) over **6j** (**6j**I: ΔH_f° = 66.79 kcal mol^{-1}; μ = 3.39 D; **6j**O: ΔH_f° = 64.75 kcal mol^{-1}; μ = 3.82 D) but it does not reproduce the clear-cut prevalence of **6a** (**6a**I: ΔH_f° = 52.58 kcal mol^{-1}; μ = 3.30 D; **6a**O: ΔH_f° = 53.56 kcal mol^{-1}; μ = 3.77 D) over **8a** (ΔH_f° = 52.48 kcal mol^{-1}; μ = 3.60 D). As for **14** (**14a**I: ΔH_f° = 57.35 kcal mol^{-1}; μ = 3.60 D; **14a**O: ΔH_f° = 57.75 kcal mol^{-1}; μ = 3.31 D; **14j**I: ΔH_f° = 70.98 kcal mol^{-1}; μ = 3.52 D; **14j**O: ΔH_f° = 70.82 kcal mol^{-1}; μ = 3.59 D), they are correctly predicted less stable than both **6** and **8**. Notice that the calculated dipole moments cannot satisfactorily explain the observed solvent polarity effect on the **6/8** ratio.
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