REACTIONS OF *O,O'*-DISUBSTITUTED BENZONITRILE OXIDES WITH 8-AZAHEPTAFULVENES[1,*]

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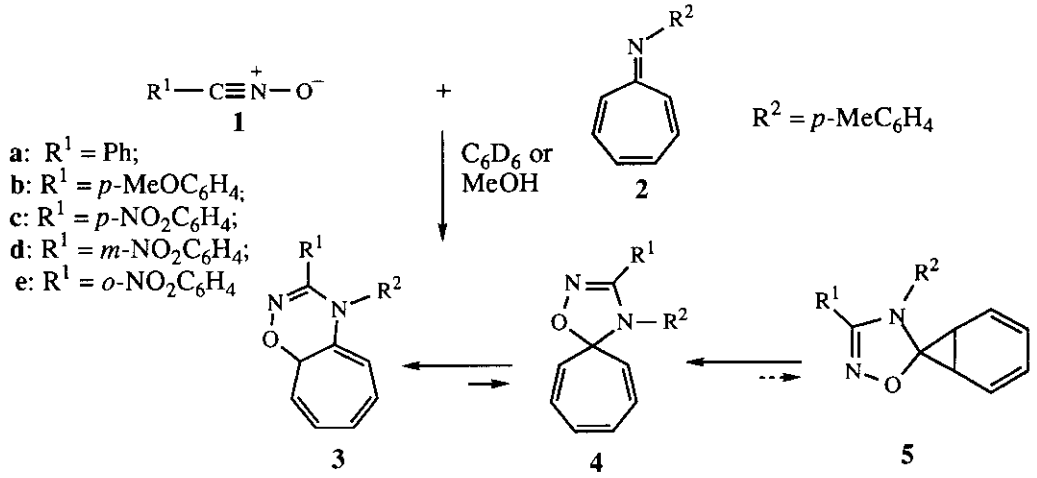
Abstract - In the reaction of *O,O'*-disubstituted benzonitrile oxides (**1f-h**) with 8-*p*-tolyl-8-azaheptafulvene (**2**) in cyclohexane there is a competition between attack by the nitrile oxides on the C=N moiety [to give a mixture of equilibrating "fused" and "spiro" adducts (**3/4**)] and on the C_2-C_3 double bond (to give **12** which isomerizes to **13**) of **2**. Site selectivity was highly enhanced by carrying out the reaction in polar solvents. Only the attack on the C=N moiety was observed in the polar and protic methanol. A synthesis of **13** by a mild new procedure of decomplexation of the tricarbonyliron complex of **12** (i.e., **15**) is described.

INTRODUCTION

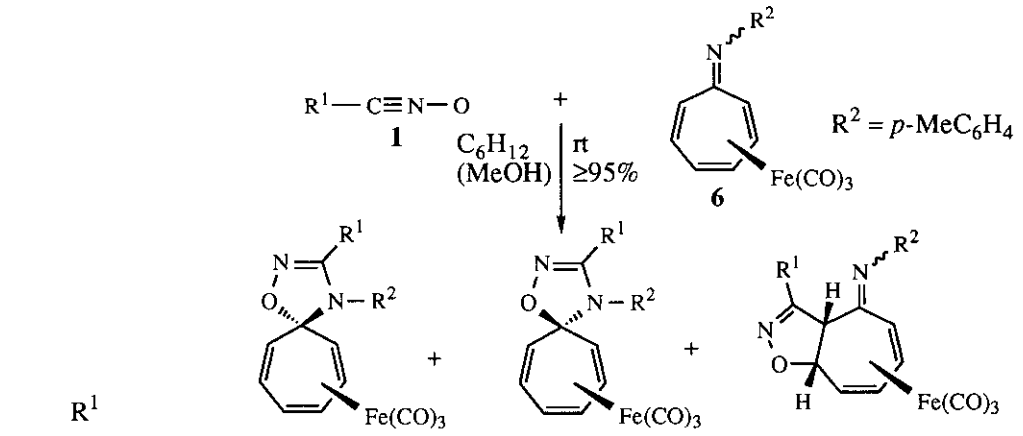
We have recently found that benzonitrile oxide and *o*-, *m*-, and *p*-monosubstituted benzonitrile oxides (**1a-e**) react readily with 8-*p*-tolylazaheptafulvene [2,4,6-cycloheptatriene-1-(*p*-tolylimine)] (**2**) to give almost quantitative yields of adducts which consist of rapidly equilibrating mixtures of "fused" **3a-e** and "spiro" **4a-e** adducts (Scheme 1).[2] The reaction takes place only at the C=N double bond of **2** (both in methanol and benzene or cyclohexane) with the carbon atom of the nitrile oxide attacking the nitrogen atom of **2** in a highly asynchronous transition state. Chemical reactivity of **3/4** suggested the presence of the norcaradiene isomer (**5**) in equilibrium with **4**.

We also observed a dramatic change in site selectivity of the reaction of nitrile oxides with the tricarbonyliron complex of **2**, i.e. **6**, (in cyclohexane at room temperature) on passing from benzonitrile oxide (R^1 = Ph) to *O,O'*-disubstituted benzonitrile oxides (R^1 = 2,6-$Cl_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 2,4,6-Me_3-3,5-Cl_2C_6) (Scheme 2).[3] In the case of benzonitrile oxide (as well as *para* and *meta* monosubstituted benzonitrile oxides) almost only the adducts on the C=N double bond were formed while with *O,O'*-disubstituted benzonitrile oxides the attack on the free C=C double bond clearly prevailed over that one on the C=N bond.[3] Moreover, a very large solvent effect (actually the largest solvent effect reported to date on selectivities of 1,3-dipolar cycloadditions)[4] on site selectivity was observed upon going from cyclohexane to

*Dedicated to Dr. Koji Nakanishi on the occasion of his 75th birthday.



Scheme 1



R^1			
a: Ph	85%[a] (75%)[b]	10% (25%)	5% (0%)
f: 2,6-$Cl_2C_6H_3$	20% (69%)	3% (27%)	77% (4%)
g: 2,4,6-$Me_3C_6H_2$	11% (67.5%)	2% (24%)	87% (8.5%)
h: 2,4,6-Me_3-3,5-Cl_2-C_6	9% (59%)	1% (23.5)	90% (17.5%)

[a]In cyclohexane [b]In methanol

Scheme 2

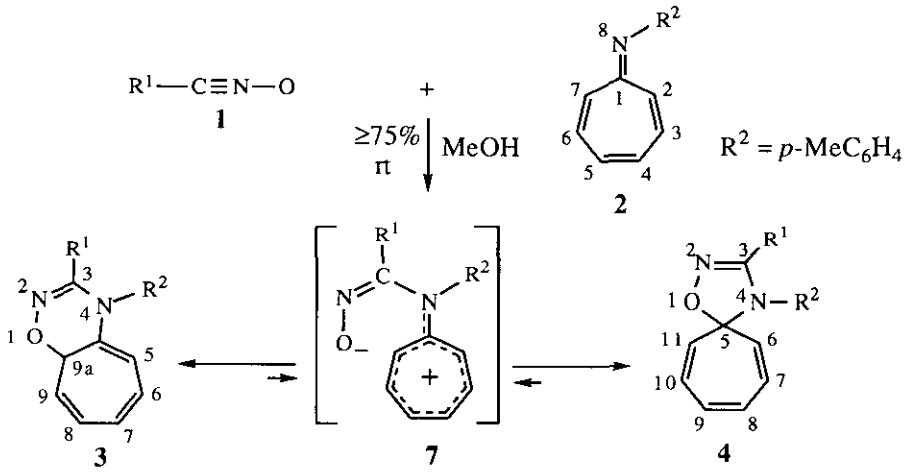
methanol (Scheme 2):[3] in the latter solvent (values in parentheses) the attack on the C=N bond was highly prevalent over that on the C=C bond for all the nitrile oxides.

These observations led us to investigate whether the change in site selectivity induced by the introduction of substituents in the *O,O'* positions of benzonitrile oxide as well as the polarity solvent effect on site selectivity hold also for the reactions of nitrile oxides with uncomplexed **2**.

RESULTS

The reaction of *O,O'*-disubstituted benzonitrile oxides (**1f-h**) with **2** took place readily (for example in case of **1f** it went to completion in ≤ 1.0 h) in methanol at room temperature (≈ 21 °C) to afford, in a site specific reaction, only adducts resulting from attack of the nitrile oxide to the C=N moiety of **2**. These adducts consisted of an inseparable mixture (NMR analysis) of interconverting "fused" (i.e., **3**) and "spiro" (i.e., **4**) isomers whose equilibrium ratio is solvent dependent. Going from deuterobenzene to deuteroacetonitrile adds a favor of 0.3-0.8 kcal mol^{-1} to the "spiro" form (Scheme 3).

An exhaustive discussion of ^{1}H NMR and ^{13}C NMR data of these types of adducts was reported in our previous paper[2] and need not be repeated in details. In short, for example, there are only five olefinic protons in compound (**3f**) and the presence of a β-enaminic residue in this isomer is revealed by the shift to high field of one olefinic proton [δ ($CDCl_3$) 5.18 (m, H-5, $J_{5,6}$ = 6.0 Hz, $J_{5,7}$ = $J_{5,9}$ = $J_{5,9a}$ = 0.5 Hz, $J_{5,8}$ = 1.0 Hz) and one olefinic carbon [δ ($CDCl_3$) 100.2 (d, C-5)] while that of an HCO moiety is supported by the signals at δ 3.76 (m, H-9a, $J_{5,9a}$ = 0.5 Hz, $J_{8,9a}$ = 1.7 Hz and $J_{9,9a}$ = 5.0 Hz) and δ 73.4 (d, C-9a) in the ^{1}H and ^{13}C NMR spectra, respectively. The singlet at δ ($CDCl_3$) 99.9 attributable to the "spiro" carbon C-5 is typical for isomer (**4f**).



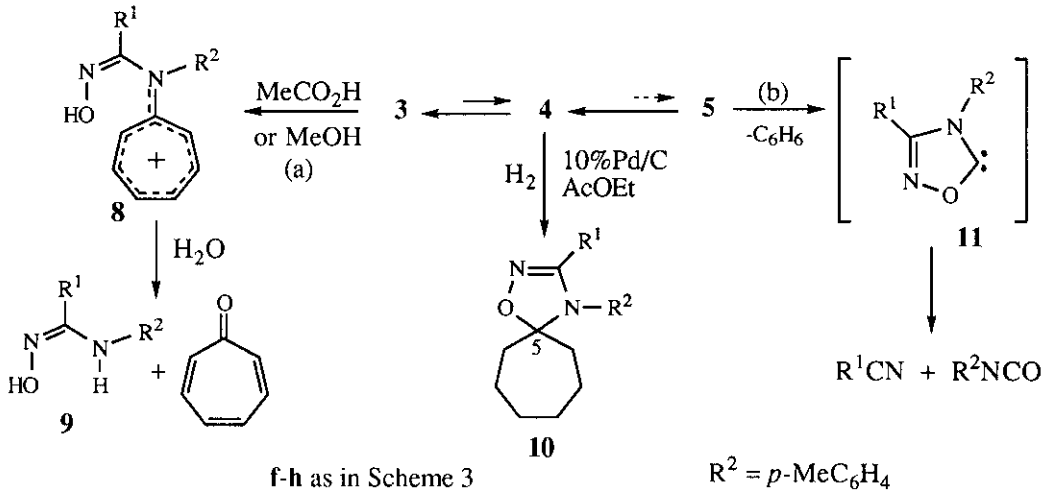
[a]Ratios **3/4** at equilibrium in C_6D_6 [b] In CD_3CN

Scheme 3

The equilibrium **3/4** is slow on the NMR time scale and the signals of both isomers are reasonably sharp at room temperature (≈ 20 °C) both in deuterobenzene and deuteroacetonitrile. Low spin saturation transfer[5] was observed in C_6D_6 by irradiating H-5 or H-9a of **3f** (i.e., the relative intensity of the signals of H-9a and

H-5, respectively, in **3f** decreased by ≈ 10%) but in deuteroacetonitrile the interconversion rate increased and spin saturation transfer was larger [i.e., a decrease in intensity (≥ 40%) of the signals of H-9a and H-5, respectively, in **3f** as well as of the signal of H-6 and H-11 in **4f** was observed upon irradiation of H-5 or H-9a of **3f** in this solvent). The latter observation is easily understandable as the equilibrium between compounds (**3**) and (**4**) must necessarily involve a zwitterion of type (**7**) as intermediate and interconversion is consequently strongly accelerated in polar solvents. As a result the exchange involving H-5 and H-9a of **3** as well as H-6 and H-11 of **4** becomes fast enough to be clearly observed by spin saturation transfer technique.

Interconversion between **3** and **4** is fast on the "chemical reaction rate" scale. For example, catalytic hydrogenation of **3f/4f** [whose equilibrium is heavily shifted (Scheme 3) to the side of the "fused" form **3f**] with Pd/C (10%) in ethyl acetate produced the sole hexahydro derivative (**10**) of the "spiro" isomer (**4f**) in high yield (Scheme 4). The easy formation of the zwitterion (**7**) (or of its protonated form, i.e., **8**) is demonstrated by the hydrolitic cleavage of **3f/4f** in acetic acid or methanol [(a), Scheme 4] at room temperature to give amidoximes (**9**) and tropone.[6]

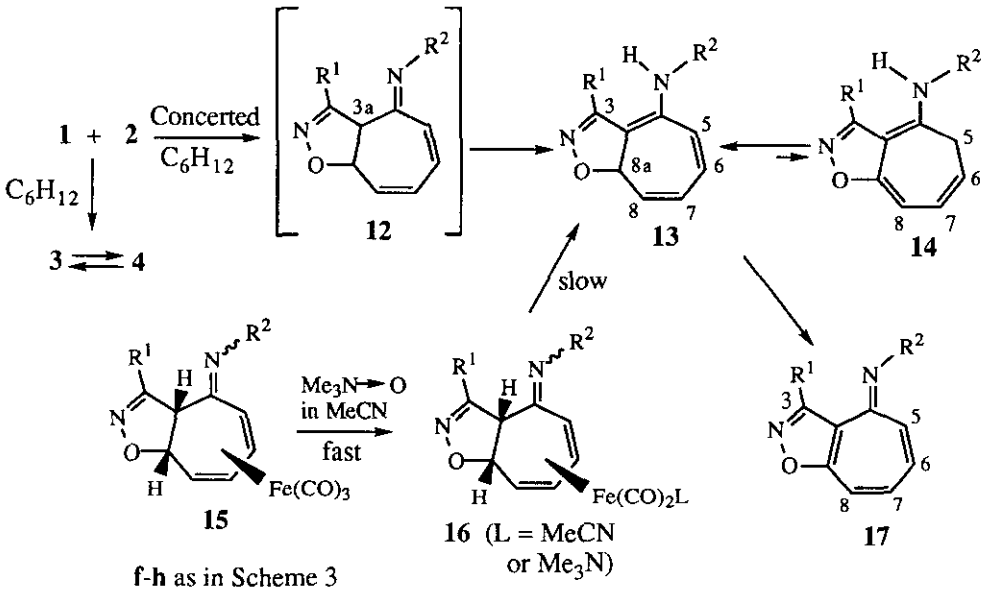


Scheme 4

The presence of the norcaradiene isomer (**5**) (which could not be detected by NMR analysis) in equilibrium with **4** is strongly supported by the thermal decomposition of **3/4** mixtures to nitriles and *p*-tolyl isocyanate most probably through the unstable 4,5-dihydro-1,2,4-oxadiazol-5-ylidene (**11**) [(b), Scheme 4)][7] formed from **5** by loss of benzene. This thermal decomposition was slow at room temperature for adducts (**3f/4f**) and adducts (**3h/4h**) but took place easily for adducts (**3g/4g**). For example, the signal of benzene (one of the decomposition products) was always present in the ^{1}H NMR spectra of **3g/4g** in $CDCl_3$ and CD_3CN and a conversion of ≈ 50% was observed for solutions of **3g/4g** in these two solvents (as well as in $CDCl_3$) kept at ≈ 21 °C for 6 days.[8]

All the above reactions of adducts from **1f-h** and **2** closely parallel those of the adducts from nitrile oxides **(1a-e) and the same dipolarophile previously reported by us.**[2]

The reaction of **2** with *O,O'*-disubstituted benzonitrile oxides (**1f-h**) in cyclohexane (at ≈ 21 °C) was slower (e.g., the reaction of **1f** with **2** went to completion in ≥ 12 h) and gave rise to a more complex product mixture (Scheme 5) than that in methanol. In particular, a yellow product, with R_f higher than that of the **3/4** adduct mixture, was present in all these reactions. The reactions with **1f** (R^1 = 2,6-$Cl_2C_6H_3$) and **1h** (R^1 = 2,4,6-Me_3-3,5-Cl_2C_6) under these conditions were clean (total yield, 92% and 75%, respectively) and column chromatography allowed easy separation of the yellow product (relative yield, 7% and 32%, respectively) from the **3/4** mixture (93% and 68%, respectively). In the case of mesitonitrile oxide (**1g**) (R^1 = 2,4,6-$Me_3C_6H_2$) the addition reaction was accompanied by thermal decomposition of **3g/4g** with formation of *p*-tolylisocyanate (according to the mechanism of Scheme 4) which in turn reacted with **2** to give the known [8+2] adduct.[2,9] However, also for **1g** there was a significant formation of the yellow product (25%) even if also in this case the attack at the C=N site was dominant (75%; total yield: 65%).



Scheme 5

The structure of the yellow adduct was established as **13** on the basis of IR and NMR spectra and chemical data. For example in the case of **13f**, the presence of an N-H bond was revealed by an absorption at 3420 cm^{-1} in the IR spectrum and by a broad singlet (which exchanged slowly, for it is shielded by the R^1 group, with D_2O) at δ($CDCl_3$) 5.08 in the ^1H NMR spectrum. The other ^1H NMR data of the yellow compound from the reaction of **1f** are fully consistent with structure (**13f**) and allowed us to definitely discard structure (**12f**) [**13f**: δ($CDCl_3$) 2.12 (s, Me), 5.18 (dd, H-8a, $J_{7,8a}$ = 2.3 Hz, $J_{8,8a}$ = 2.7 Hz), 5.74 (dddd, H-8, $J_{5,8}$ = 0.8 Hz, $J_{6,8}$ = 0.4 Hz , $J_{7,8}$ = 10.3 Hz, $J_{8,8a}$ = 2.7 Hz), 6.09 (ddd, H-7, $J_{6,7}$ = 5.6 Hz, $J_{7,8}$ = 10.3 Hz, $J_{7,8a}$ = 2.3 Hz), 6.41 (br d, H-5, $J_{5,6}$ = 11.7 Hz), 6.53 (br dd, H-6, $J_{5,6}$ = 11.7 Hz, $J_{6,7}$ = 5.6 Hz), 6.38 and 6.79 (AA'XX' system of the p-tolyl group), 7.11(dd, 1 H, aromatic proton, J = 8.0 and 1.5 Hz), 7.15 (t, 1 H, J = 8.0 Hz, aromatic proton), 7.35 (dd, 1H, aromatic proton, J = 8.0 and 1.5 Hz)]. In

particular, it is evident the absence of protons of the type H-3a of **12** and the presence of a deshielded saturated proton (H-8a) which is flanking a system of four diene protons as in **13**. Moreover, the doublet at $\delta(CDCl_3)$ 81.0 in the (off resonance) ^{13}C NMR spectrum is a diagnostic feature for the deshielded saturated carbon at position 8a in **13f**. The three signals for the three protons of the $Cl_2C_6H_3$ group indicate that this group (the R^1 group) can not rotate freely but is locked in an out-of-plane conformation in which the two meta protons are not equivalent.

Compounds (**13**) were always accompanied by variable minor amounts (1-10%) of an inseparable isomer for which we suggest structure (**14**). In fact, the ^1H NMR spectrum of this isomer is characterized by a double doublet [**14f**, δ ($CDCl_3$) 3.42 (dd, 2 H, H-5, $J_{5,6}$ = 6.0 Hz and $J_{5,7}$ = 0.8 Hz)] attributable to a methylene group, by a broad singlet (δ 4.88, 1 H, NH, exchangeable with D_2O) and by the signals of three vinyl protons one of which is coupled to the methylene group through a vicinal coupling constant [δ 5.29 (dt, 1 H, H-6, $J_{5,6}$ = 6.0 Hz and $J_{6,7}$ = 10.0 Hz), 5.79 (d, 1 H, H-8, $J_{7,8}$ = 6.8 Hz), 6.01 (ddt, 1 H, H-7, $J_{6,7}$ = 10.0 Hz, $J_{7,8}$ = 6.8 Hz, $J_{5,7}$ = 0.8 Hz)]. Compounds (**14**) can derive from **13** through a thermally allowed suprafacial [1,5-H] sigmatropic shift however we feel that their formation is the result of a catalyzed (e.g., by silicagel) process.

At this point it was mandatory to synthesize compounds (**13**) by oxidative degradation of compounds (**15**)[3] possibly by using a mild oxidant[10,11] to avoid further oxidation of **13**. Compounds (**15**) entered a fast (less than 15 min) oxidation reaction in the presence of excess trimethylamine-*N*-oxide in acetonitrile with formation of a new yellow product (TLC analysis). In the case of the reaction of **15f** (R^1 = 2,6-$Cl_2C_6H_3$) this compound could be made precipitate as beautiful orange-yellow crystals by carrying out the oxidation in concentrated solution. The two strong broad bands in the IR spectrum [ν_{max} (Nujol) 1945 and 1998 cm^{-1} to be compared to ν_{max} (Nujol) 1980, 1998 and 2065 cm^{-1} for **15f**] showed that it still contains an $Fe(CO)_x$ moiety. Elemental analysis was more consistent with a complex in which one CO group had been replaced by one MeCN molecule (i.e., L = MeCN) than with a trimethylamine ligand (i.e., L = Me_3N). This complex decomposed rapidly when dissolved in acetone, dicloromethane, chloroform, benzene but it was relatively stable in acetonitrile or even, for example, in dichloromethane/acetonitrile. We could not obtain good ^1H NMR spectra of this compound; even in deuterodichloromethane/deuteroacetonitrile the signals were broad and unresolved. Structure (**16f**) (L = MeCN) seems to be a reasonable candidate for this intermediate. Further oxidative decomposition of **16f** was much slower and oxidation of **13f** came into play. After several days the completely oxidized derivative (**17f**) was isolated in good yields. A serendipitous observation led us to solve the problem of removing the tricarbonyliron group from **15f** however without interference of further oxidation of **13f** to **17f**. In one instance after half an hour the acetonitrile solution was diluted with carbon tetrachloride and washed with water to remove excess trimethylamine-*N*-oxide. To our surprise, no complex (**16f**) could be detected by TLC analysis of the organic layer but aside from small amounts of **17f** the only important spot was that of **13f** which was easily isolated in fair yields by column chromatography. Likewise, synthesis of **13g** and **13h** was achieved by diluting (after 30 min) the oxidation mixture of **15g** and **15h**, respectively, with carbon tetrachloride.

Compounds (**13**) prepared according to this procedure were also contaminated by small amounts of compounds (**14**).

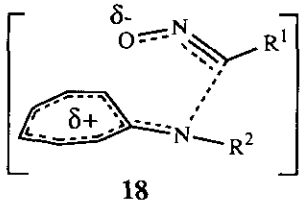
This synthesis definitely proved structure (**13**) and, consequently, the presence of substantial amounts of attack to the C_2-C_3 double bond of **2** by *O,O'*-disubstituted benzonitrile oxides to give **12** which rapidly tautomerizes to **13**.

Coming back to the cycloaddition reaction, the reaction of **1h** with **2** was carried out also in acetonitrile a strongly polar aprotic solvent. Site selectivity was strongly increased with respect to the reaction in cyclohexane but without reaching site specificity as in the reaction in methanol (total yield 82%; **3h+4h**:**13h+14h** ≈ 97:3).

To conclude, our results confirm that also in the reactions of **2**, as in those of **6**, there is a higher tendency of *O,O'*-disubstituted benzonitrile oxides with respect to *o*, *m* and *p*-monosubstituted benzonitrile oxides to react with the C_2-C_3 double bond. The former nitrile oxides evidently experience a higher steric retardation of their attack to the C=N double bond as compared to that to the C_2-C_3 double bond. As a result the reaction of the latter bond tends to become competitive with the former one.

However, in the reactions of **2** (in contrast to the reactions of **6**, Scheme 2) the attack on the C=N moiety remains dominant over that on the C=C bond even with *O,O'*-disubstituted benzonitrile oxides in cyclohexane. This means that positive charge stabilization by the cycloheptatriene moiety of **2** (i.e., its tendency to favor a highly asynchronous TS in which there is a moiety which closely resembles a tropylium ion as in **18**) is very strong. In particular, it is stronger than the related ability of the irontricarbonyl cycloheptatriene moiety of **6** to stabilize a positive charge (as in **19**).

The solvent effect on site selectivity of the reaction of **1f-h** is in accord with a development of relevant partial charges on the two interacting partners in the TS of the attack (i.e., **18** in which formation of the



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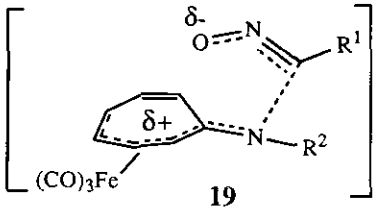

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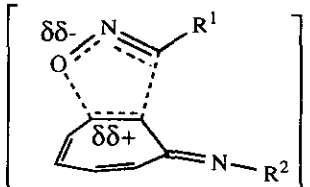

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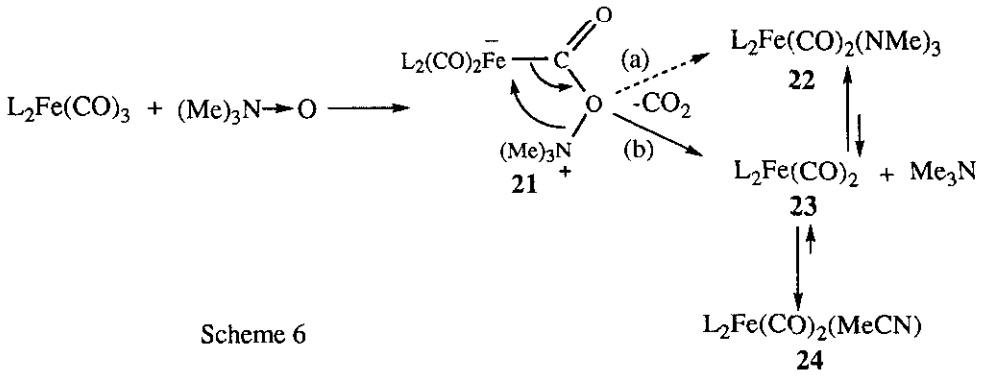
bond between the oxygen and C-1 of **2** might have not started yet) on the C=N moiety. Moreover, charge transfer should be less pronounced in TS (**20**), leading to **12**, which is more synchronous than TS (**18**).

Solvent effect on site selectivity is certainly strong even if it could not be exactly evaluated for in methanol adduct (**13**) is below the detection limits (≈2%) of our analytic techniques. From a synthetic standpoint it is remarkable that by changing the solvent one can made the reaction of *O,O'*-disubstituted benzonitrile oxides become fast (on passing from cyclohexane to methanol absolute reaction rate increases by ≥ 10 times), clean and site specific (with formation of the sole **3/4** mixture).

As for the decomplexation reaction, a short comment is in order also on the mechanism of this reaction. Oxidation of iron carbonyl complexes with trimethylamine-*N*-oxide is often described as following path (a)

of Scheme 6.[11,12] Curved arrows in **21** suggest that the reaction ends up [dashed arrow, mechanism (a)] directly with formation of the complex (**22**) in which one carbonyl group has been replaced by a trimethylamine molecule. Actually, decomposition of **21** follows the alternative mechanism (b)[11,13] with initial formation of the unsaturated complex (**23**) which can then be trapped by a ligand to give a coordinatively saturated complex. This hypothesis is supported by our observation that treating a solution of $Fe(CO)_5$ in acetonitrile with trimethylamine-*N*-oxide while bubbling a stream of argon afforded complex (**24**) [$L_2 = (CO)_2$] (and not **22**) as the highly dominant product. A ≈ 1:1 mixture of **22** [$L_2 = (CO)_2$] and **24** [$L_2 = (CO)_2$] was formed when this reaction was carried out in acetonitrile solution saturated with trimethylamine. Complex (**22**) [$L_2 = (CO)_2$] did not transform appreciably into complex (**24**) [$L_2 = (CO)_2$]



Scheme 6

when dissolved in acetonitrile while **24** [$L_2 = (CO)_2$] (generated photochemically from $Fe(CO)_5$ in acetonitrile)[14] was slowly transformed into **22** [$L_2 = (CO)_2$] when its acetonitrile solution was saturated with trimethylamine. These data demonstrate that complex (**22**) is much more stable than **24** but also that there is formation of the coordinatively unsaturated **23** which is very reactive and is rapidly trapped also by weak ligands (such as MeCN to give **24**).

In the decomplexation of **15** the coordinatively unsaturated intermediate of the type (**23**) is apparently trapped only by the weaker ligand MeCN to give **16** (L = MeCN) and not by Me_3N. This hypothesis needs more convincing proofs and we are now investigating the decomplexation by trimethylamine-*N*-oxide of other η^4-diene-tricarbonyliron complexes in order to produce new data useful to solve this problem. Anyway, fast oxidation with formation of a new complex with broad strong absorptions at ≈ 1940 and 2000 cm^{-1} seems to be a general behavior for η^4-diene-tricarbonyliron complexes.[15]

As for the decomposition of **16** promoted by carbon tetrachloride it has a precedent in literature in a finding by Hogeveen and Elzinga who described the decomposition of the complex (**22**) by CCl_4.[12] They proposed that this reaction involves dissociation of **22** to **23** which then abstracts a chlorine atom from CCl_4 with formation of $CCl_3^{\bullet}$ and **25**. A complex of the type (**25**) can be proposed also for the first step of the

$$\underset{\mathbf{23}}{L_2Fe(CO)_2} + CCl_4 \longrightarrow CCl_3 + \underset{\mathbf{25}}{L_2Fe(CO)_2Cl}$$

decomposition of compounds (**16**) by carbon tetrachloride (which terminates with formation of compounds **13**) but at present we have no data to suggest further details for the mechanism of this reaction.

Anyway, the reaction of dienetricarbonyliron complexes with trimethylamine-*N*-oxide in acetonitrile followed by treatment with carbon tetrachloride provides a mild and interesting method for decomplexation of substrates which may be sensitive to further oxidation.

EXPERIMENTAL

Melting points are uncorrected and were measured with a Büchi 535 apparatus. Elemental analyses were made on a Carlo Erba CHN analyzer, model 1106. IR 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 300.13 and 75.47 MHz, respectively) spectrometer with tetramethylsilane as internal standard at 20 °C for $CDCl_3$, C_6D_6 and CD_3CN solutions. The ^1H NMR spectra in CD_3CN were very similar to those in $CDCl_3$ while in C_6D_6 chemical shifts (both absolute and relative values) were different. However, the diagnostic features of these spectra are independent of the solvent used. Protons were correlated by decoupling experiments. Assignments were secured by $^1H/^{13}C$ heterocorrelated spectra. ^1H NMR spectra were evaluated as first order spectra). In the case of compounds (**4**) the olefinic protons (H-6, H-7, H-8, H-9, H-10 and H-11) constitute a complex AA'BB'CC' system and coupling constants could not be evaluated.

GC analyses were carried out with a DANI 6500, PTV injector, CP-Sil-19CB (25 m) capillary column and carrier H_2. TLCs were done on plates precoated with silicagel 60 GF_{254} (Merck). Spots were visualized either by spraying with 3% chromic oxide in sulfuric 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 benzene and cyclohexane/ethyl acetate (in particular cyclohexane/ethyl acetate = 9:1) mixtures.

Nitrile oxides(**1f-h**)[16] and azaheptafulvene (**2**)[17] were prepared according to literature procedures.

Reactions of nitrile oxides (1f), (1g) and (1h) with azaheptafulvene (2). A solution of nitrile oxides (**1f**), (**1g**) and (**1h**), respectively, (1.2 mmol) and of **2** (1.0 mmol) in methanol (10 mL) was left at rt (≈ 21 °C) under argon until TLC analysis showed the complete disappearance of **2** (≤1.0 h for **1f**, ≤15 h for **1g** and ≤ 8 h for **1h**). TLC analysis showed also that the reactions were clean and no significant amounts of yellow adducts (i.e., **13**) were present in the reaction mixtures. Cooling the reaction mixture at -20 °C allowed isolation of adducts (**3f/4f**) (≥ 65%) and of adducts (**3h/4h**) (≈ 80%) as crystalline products. Further amounts of products were isolated by column chromatography with total yields of 87% and 90%, respectively, for **3f/4f** and **3h/4h**. In the case of the reaction of mesitonitrile oxide adducts (**3g/4g**) were isolated in 85% yield by column chromatography as colorless viscous oil. Owing to easy decomposition of **3g/4g** we could not obtain good elemental analysis for this mixture.

3f/4f: slightly yellow prisms from methanol, mp 96-99 °C (decomp) (Anal. Calcd for $C_{21}H_{16}N_2OCl_2$: C, 65.8 ; H, 4.2; N, 7.3. Found: C, 65.5; H, 4.4; N, 7.6.). **3f**: ^1H NMR δ (ppm, $CDCl_3$) 2.22 (s, Me), 3.76 (m, H-9a, $J_{5,9a}$ = 0.5 Hz, $J_{8,9a}$ = 1.7 Hz, $J_{9,9a}$ = 5.0 Hz), 5.18 (m, H-5, $J_{5,6}$ = 6.0 Hz, $J_{5,9} \approx J_{5,9a} \approx J_{5,7} \approx$

0.5 Hz), 6.18 (m, H-9, $J_{5,9} \approx J_{6,9} \approx J_{7,9} \approx 0.5$ Hz, $J_{8,9} = 9.5$ Hz), 6.31 (m, H-8, $J_{5,8} = 1.0$ Hz, $J_{6,8} = 1.0$ Hz, $J_{7,8} = 4.8$ Hz, $J_{8,9} = 9.5$ Hz), 6.51 (m, H-6, $J_{5,6} = 6.0$ Hz, $J_{6,7} = 11.0$ Hz, $J_{6,8} = 1.0$ Hz, $J_{6,9} \approx 0.5$ Hz), 6.56 (m, H-7, $J_{6,7} = 11.0$ Hz, $J_{5,7} \approx J_{7,9} \approx 0.5$ Hz), 6.9-7.4 (aromatic protons); δ (ppm, CD_3CN) 2.21 (s, Me), 3.71 (m, H-9a), 5.11 (m, H-5), 6.09 (m, H-9), 6.34 (m, H-8), 6.52 (m, H-6) 6.61 (m, H-7); δ (ppm, C_6D_6) 1.75 (s, Me), 4.05 (m, H-9a), 5.21 (m, H-5), 6.18 (m, H-8), 6.35 (m, H-6 and H-7), 6.52 (m, H-9) ; ^{13}C NMR δ (ppm, $CDCl_3$) 21.0 (q, Me), 73.4 (d, C-9a), 100.2 (d, C-5), 122.9 (d, C-9), 124.4 (d, C-8), 127.3 (d, C-7), 128.9 (d, C-6), 148.1 (s, C-3). **4f**: ^1H NMR δ (ppm, $CDCl_3$) 2.20 (s, Me), 6.22 (m, H-6 and H-7); δ (ppm, CD_3CN) 2.18 (s, Me), 6.19 (m, H-6 and H-11), 6.37-6.50 (m, H-7, H-8, H-9 and H-10); δ (ppm, C_6D_6) 1.80 (s, Me), 5.95 (m, 2H, H-8 and H-9); the signals of protons of **4f** not reported (in all the three solvents) are buried under the signals of **3f**; ^{13}C NMR δ (ppm, $CDCl_3$) 20.5 (q, Me), 99.9 (s, C-5).

Ratios **3f/4f** were the following: 92:8 (C_6D_6), 85:15 ($CDCl_3$) and 75:25 (CD_3CN).

The intensity ratios between the signals (in CD_3CN) of the interconverting protons [H-5 and H-9a of **3f** and H-6 and H-11 of **4f**] changed from 1.0 (H-9 of **3f**, taken as reference proton since it is not involved in exchange with the irrradiated protons):1.0 (H-5):1.0 (H-9a):0.66 (H-6 + H-11) to 1.0 (H-9):0.5 (H-9a):0.2 (H-6 + H-11) upon irradiation of H-5 and to 1.0 (H-9):0.6 (H-9a):0.3 (H-6 + H-11).upon irradiation of H-9a. In contrast, upon irradiation of H-5 and H-9a, respectively, of **3f** in C_6D_6 the intensity decrease of H-9a and H-5, respectively, was ≈ 10%.

3g/4g: colorless viscous oil; **3g**: ^1H NMR δ (ppm, $CDCl_3$) 2.12 (s, Me), 2.21 (s, Me) and 2.31 (s, two Me), 3.77 (m, H-9a, $J_{5,9a} = 0.7$ Hz, $J_{8,9a} = 1.5$ Hz, $J_{9,9a} = 5.0$ Hz), 5.09 (m, H-5, $J_{5,6} = 5.8$ Hz, $J_{5,7} \approx J_{5,9} \approx 0.6$ Hz, $J_{5,8} = 1.0$ Hz, $J_{5,9a} = 0.7$ Hz), 6.16 (m, H-9, $J_{5,9} \approx J_{6,9} \approx J_{7,9} \approx 0.6$ Hz, $J_{8,9} = 9.5$ Hz, $J_{9,9a} = 5.0$ Hz), 6.31 (m, H-8, $J_{5,8} = 1.0$ Hz, $J_{6,8} = 1.5$ Hz, $J_{7,8} = 5.0$ Hz, $J_{8,9a} = 1.5$ Hz), 6.50 (m, H-6, $J_{5,6} = 5.8$ Hz, $J_{6,7} = 10.5$ Hz, $J_{6,8} = 1.5$ Hz, $J_{6,9} \approx 0.6$ Hz), 6.55 (m, H-7, $J_{6,7} = 10.5$ Hz, $J_{5,7} \approx J_{7,9} \approx 0.6$ Hz, $J_{7,8} = 5.0$ Hz), 6.68 and 6.83 (AA'XX' system, *p*-$MeC_6\underline{H}_4$), 6.79 (s, 2 H, aromatic protons); ^{13}C NMR δ (ppm, $CDCl_3$) 73.2 (d, C-9a), 99.7 (d, C-5), 151.7 (s, C-3); δ (ppm, CD_3CN) 73.0 (d, C-9a), 99.8 (d, C-5), 151.3 (s, C-3). **4g**: ^1H NMR δ (ppm, $CDCl_3$) 2.17 (s, Me), 2.22 (s, Me), 2.34 (s, two Me), 6.13 (m, H-6 and H-11), 6.42 (m, H-7, H-8, H-9 and H-10), 6.61 (s, 2 H, aromatic protons), 6.92 and 6.98 (AA'XX' system, *p*-$MeC_6\underline{H}_4$); ^{13}C NMR δ (ppm, $CDCl_3$) 98.1(s, C-5), 151.4 (s, C-3); δ (ppm, CD_3CN) 98.5 (s, C-5), 151.4 (s, C-3).

In the ^1H NMR spectrum are present also three singlets at δ 2.31 (Me), 2.49 (Me) and 7.46 (C_6H_6) attributable to p-tolylisocyanate, mesitonitrile and benzene deriving from thermal decomposition of **3g/4g** *via* **5g** and **11g**.

Ratios **3g/4g** were the following: 46:54 (C_6D_6), 44:56 ($CDCl_3$) and 31:69 (CD_3CN).

3h/4h: slightly yellowish-brownish prisms from methanol/benzene, mp 139-140 °C (decomp); (Anal. Calcd for $C_{24}H_{22}N_2OCl_2$: C, 67.8; H, 5.2; N, 6.6. Found: C, 67.9; H, 5.3; N, 6.8.). **3h**: ^{1}H NMR δ (ppm, $CDCl_3$) 2.17, 2.23, 2.37 and 2.54 (four s, Me), 3.74 (m, H-9a, $J_{5,9a}$ = 0.5 Hz, $J_{8,9a}$ = 1.5 Hz, $J_{9,9a}$ = 5.0 Hz), 5.11 (br d, H-5, $J_{5,6}$ = 6.0 Hz), 6.15 (m, H-9, $J_{5,9} \approx J_{6,9} \approx J_{7,9} \approx$ 0.7 Hz, $J_{8,9}$ = 9.5 Hz, $J_{9,9a}$ = 5.0 Hz), 6.33 (m, H-8, $J_{5,8} \approx J_{6,8} \approx$ 1.0 Hz, $J_{7,8}$ = 5.5 Hz, $J_{8,9}$ = 9.5 Hz, $J_{8,9a}$ = 1.5 Hz), 6.51 (m, H-6, $J_{5,6}$ = 6.0 Hz, $J_{6,7}$ = 11.0 Hz, $J_{6,8} \approx$ 1.0 Hz, $J_{6,9} \approx$ 0.7 Hz), 6.56 (m, H-7, $J_{5,7}$ = 1.0 Hz, $J_{6,7}$ = 11.0 Hz, $J_{7,8}$ = 5.5 Hz, $J_{7,9} \approx$ 0.7 Hz), 6.89 and 7.00 (AA'XX' system, *p*-Me$C_6\underline{H}_4$); δ (ppm, CD_3CN) 3.71 (m, H-9a), 5.08 (m, H-5), 6.11 (m, H-9), 6.35 (m, H-8), 6.57 (m, H-6), 6.60 (H-7); δ (ppm, C_6D_6) 4.01 (m, H-9a), 5.11 (m, H-5), 6.19 (m, H-9), 6.45 (m, H-6, H-7 and H-8); ^{13}C NMR δ (ppm, $CDCl_3$) 18.7, 19.1, 19.3 and 20.9 (four q, four Me), 73.1 (d, C-9a), 100.4 (d, C-5), 122.3 (d, C-9), 124.9 (d, C-8), 127.5 (d, C-7), 129.1 (d, C-6), 150.9 (s, C-3). **4h**: 2.16 (s, Me), 2.40 (s, two Me), 2.55 (s, Me), 6.12 (m, H-6 and H-11), 6.30-6.50 (m, H-7, H-8, H-9 and H-10), 6.72 and 6.83 (AA'XX' system, *p*-Me$C_6\underline{H}_4$); δ (ppm, CD_3CN) 6.15 (m, H-6 and H-11), 6.35-6.50 (m, H-7, H-8, H-9 and H-10); δ (ppm, C_6D_6) 5.92 (m, H-8 and H-9), 6.05 (m, H-7 and H-10), 6.17 (m, H-6 and H-11); ^{13}C NMR δ (ppm, $CDCl_3$) 18.6 (q, two Me), 18.9 (q, Me), 20.7 (q, Me), 98.6 (s, C-5), 126.9 (d, C-6 and C-11), 127.4 (d, C-8 and C-9 or C-7 and C-10), 129.6 (d, C-7 and C-10 or C-8 and C-9), 151.4 (s, C-3).

Ratios **3h/4h** were the following: 76:24 (C_6D_6), 66:34 ($CDCl_3$) and 52:48 (CD_3CN).

The reaction of nitrile oxides (**1f**), (**1g**) and (**1h**), respectively, (1.0 mmol) with **2** (1.17 mmol) in cyclohexane (5.0 mL) was carried out under argon at ≈ 21 °C for **1f** and **1h** and at ≈ 35 °C for **1g**. The reaction of **1f** went to completion in ≈ 12 h (TLC analysis). After 20 h the solvent was evaporated and the residue column chromatographed (benzene as eluant) to give in order of elution 23 mg (6%) of **13f+(14f)** and 329 mg (86%) of **3f/4f**. The reaction of **1h** was interrupted after 60 h and usual work-up led to recovery (in order of elution, benzene as eluant) of 16 mg of **1h**, 101 mg (24%) of **13h+(14h)** and 216 mg (51%) of **3h/4h**. The reaction of **1g** was interrupted after 50 h. Column chromatography allowed isolation of 30 mg of a mixture of mesitonitrile (IR: ν_{max} 2218 cm^{-1}) and mesitonitrile oxide (IR: ν_{max} 2285 cm^{-1}), 106 mg of a mixture of **13g+14g** and of the adduct between **2** and *p*-tolyl isocyanate (whose ratio could be easily evaluated by ^{1}H NMR as 1.1:1.0; yield: 16% for **13g+14g** and 15% for adduct (**2**)-tolyl isocyanate) and 121 mg (34%) of **3g/4g**.

13f+14f: orange-yellow glassy solid; (Anal. Calcd for $C_{21}H_{16}N_2OCl_2$: C, 65.8; H, 4.2; N, 7.3. Found: C, 66.0; H, 4.0; N, 7.0.); IR (nujol) ν_{max} 3420 cm^{-1} (NH); **13f**: ^{1}H NMR δ (ppm, $CDCl_3$) 2.12 (s, Me), 5.08 (br s, NH), 5.18 (dd, H-8a, $J_{7,8a}$ = 2.3 Hz, $J_{8,8a}$ = 2.7 Hz), 5.74 (dddd, H-8, $J_{5,8}$ = 0.8 Hz, $J_{6,8}$ = 0.4 Hz , $J_{7,8}$ = 10.3 Hz, $J_{8,8a}$ = 2.7 Hz), 6.09 (ddd, H-7, $J_{6,7}$ = 5.6 Hz, $J_{7,8}$ = 10.3 Hz, $J_{7,8a}$ = 2.3 Hz), 6.41

(br d, H-5, $J_{5,6}$ = 11.7 Hz), 6.53 (br dd, H-6, $J_{5,6}$ = 11.7 Hz, $J_{6,7}$ = 5.6 Hz), 6.38 and 6.79 (AA'XX' system of the *p*-tolyl group), 7.11(dd, 1 H, J = 8.0 and 1.5 Hz, aromatic proton), 7.15 (t, 1 H, J = 8.0 Hz, aromatic proton), 7.35 (dd, 1H, aromatic proton, J = 8.0 and 1.5 Hz); ^{13}C NMR δ (ppm, $CDCl_3$) 20.4 (q, Me), 81.0 (d, C-8a), 116.8 and 129.3 (two d, four CH of *p*-MeC_6H_4), 121.5 (d, C-8), 126.4 (d, C-7), 131.4 (d, C-5), 133.9 (d, C-6), 151.6 (d, C-3), 127.7, 128.4 and 131.0 (three d, three CH of the 2,6-$Cl_2C_6H_3$ group); **14f**: ^{1}H NMR δ (ppm, $CDCl_3$) 2.18 (s, Me), 3.42 (dd, 2 H, H-5, $J_{5,6}$ = 6.0 Hz and $J_{5,7}$ = 0.8 Hz), 4.88 (br s, 1 H, NH), 5.29 (dt, 1 H, H-6, $J_{5,6}$ = 6.0 Hz and $J_{6,7}$ = 10.0 Hz), 5.79 (d, 1 H, H-8, $J_{7,8}$ = 6.8 Hz), 6.01 (ddt, 1 H, H-7, $J_{5,7}$ = 0.8 Hz, $J_{6,7}$ = 10.0 Hz, $J_{7,8}$ = 6.8 Hz).

13g+14g: yellow glassy solid; (Anal. Calcd for $C_{24}H_{24}N_2O$: C, 80.9; H, 6.8; N, 7.9. Found: C, 80.8; H, 6.9; N, 7.8.). **13g**: ^{1}H NMR δ (ppm, $CDCl_3$) 2.04, 2.22, 2.27 and 2.36 (four s, Me), 5.15 (ddd, H-8a, $J_{5,8a}$ = 0.6 Hz, $J_{7,8a}$ = 2.3 Hz, $J_{8,8a}$ = 2.7 Hz), 5.27 (br s, NH), 5.88 (dddd, H-8, $J_{5,8} \approx J_{6,8} \approx$ 0.5 Hz , $J_{7,8}$ = 10.2 Hz, $J_{8,8a}$ = 2.7 Hz), 6.12 (dddd, H-7, $J_{5,7}$ = 0.7 Hz, $J_{6,7}$ = 5.2 Hz, $J_{7,8}$ = 10.2 Hz, $J_{7,8a}$ = 2.3 Hz), 6.54 (dddd, H-5, $J_{5,6}$ = 11.7 Hz, $J_{5,7}$ = 0.7 Hz, $J_{5,8} \approx J_{5,8a} \approx$ 0.6 Hz,), 6.59 (br dd, H-6, $J_{5,6}$ = 11.7 Hz, $J_{6,7}$ = 5.2 Hz), 6.37 and 6.88 (AA'XX' system of the *p*-tolyl group), 6.74 and 6.99 (two s, aromatic proton of the mesito group); ^{13}C NMR δ (ppm, $CDCl_3$) 19.4, 19.9, 20.4 and 20.9.(four q, Me), 80.2 (d, C-8a), 117.6 and 129.3 (two d, four CH of *p*-MeC_6H_4), 121.3 (d, C-8), 127.4 (d, C-7), 131.1 (d, C-5), 132.9 (d, C-6), 154.2 (d, C-3), 128.4 and 128.8 (two d, two CH of 2,4,6-$Me_3C_6H_2$); **14g**: ^{1}H NMR δ (ppm, $CDCl_3$) 3.42 (dd, 2 H, H-5, $J_{5,6}$ = 6.0 Hz and $J_{5,7}$ = 0.8 Hz), 4.89 (br s, 1 H, NH), 5.28 (dt, 1 H, H-6, $J_{5,6}$ = 6.0 Hz and $J_{6,7}$ = 10.0 Hz),), 5.81 (d, 1 H, H-8, $J_{7,8}$ = 6.8 Hz), 6.00 (ddt, 1 H, H-7, $J_{5,7}$ = 0.8 Hz, $J_{6,7}$ = 10.0 Hz, $J_{7,8}$ = 6.8 Hz).

13h+14h: yellow prisms from petrol ether, mp 137-139 °C; (Anal. Calcd for $C_{24}H_{22}N_2OCl_2$: C, 67.8; H, 5.2; N, 6.6. Found: C, 67.8; H, 5.1; N, 6.6.); IR (nujol) ν_{max} 3420 cm^{-1} (NH); **13h**: ^{1}H NMR δ (ppm, $CDCl_3$) 2.07, 2.16, 2.43 and 2.51 (four s, Me), 5.08 (br s, NH), 5.21 (ddd, H-8a, $J_{5,8a}$ = 0.7 Hz, $J_{7,8a}$ = 2.3 Hz, $J_{8,8a}$ = 2.7 Hz), 5.86 (dddd, H-8, $J_{5,8} \approx J_{6,8} \approx$ 0.5 Hz , $J_{7,8}$ = 10.3 Hz, $J_{8,8a}$ = 2.7 Hz), 6.14 (ddd, H-7, $J_{6,7}$ = 5.6 Hz, $J_{7,8}$ = 10.3, $J_{7,8a}$ = 2.3 Hz), 6.51 (br d, H-5, $J_{5,6}$ = 11.8 Hz), 6.61 (br dd, H-6, $J_{5,6}$ = 11.8 Hz, $J_{6,7}$ = 5.6 Hz), 6.35 and 6.90 (AA'XX' system of the *p*-tolyl group); ^{13}C NMR δ (ppm, $CDCl_3$) 19.4, 19.9, 20.4 and 20.9 (four q, Me), 80.2 (d, C-8a), 117.6 and 129.3 (two d, four CH of *p*-MeC_6H_4), 121.3 (d, C-8), 127.4 (d, C-7), 131.1 (d, C-5), 132.9 (d, C-6), 154.2 (d, C-3), 128.4 and 128.8 (two d, two CH of 2,4,6-$Me_3C_6H_2$); **14h**: ^{1}H NMR δ (ppm, $CDCl_3$) 2.20 (s two Me), 2.28 (s, Me), 2.52 (s, Me), 3.52 (dd, 2 H, H-5, $J_{5,6}$ = 6.0 Hz and $J_{5,7}$ = 0.5 Hz), 4.96 (br s, NH), 5.38 (dt, 1 H, H-6, $J_{5,6}$ = 6.0

Hz and $J_{6,7}$ = 10.3 Hz),), 5.84 (d, 1 H, H-8, $J_{7,8}$ = 6.5 Hz), 6.08 (ddt, 1 H, H-7, $J_{5,7}$ = 0.5 Hz, $J_{6,7}$ = 10.0 Hz, $J_{7,8}$ = 6.8 Hz).

The ratio **13/14** was highly variable (1-10%). Conversion of **13** into **14** seems to be catalyzed by silicagel. In fact, when product separation was carried out by slow column chromatography the % of **14** increased while the lowest amounts of **14** were present in case of separations by fast column chromatography. In one experiment compound (**13h**) with ≤ 1% of **14h** was dissolved in methylene chloride, the solution absorbed on silicagel, the solvent evaporated under vacuum and the silicagel with absorbed **13h** was left for 1 h at rt. Elution with benzene led to recovery of **13h+14h** mixture in which **14h** accounted for 10% of the product. The reaction of **1h** (0.50 mmol) with **2** (0.60 mmol) was also carried out in acetonitrile (5 mL). After 48 h usual work-up led to isolation on **13h+14h** (2%) and **3h/4h** (80%).

Catalytic hydrogenation of compound (3f/4f). A solution of compound (**3f/4f**) (200 mg, 0.52 mmol) in ethyl acetate (20 mL) was hydrogenated in the presence of Pd/C (10%, 40 mg) at rt and under atmospheric pressure. After the absorption of 3.1 mol equiv. of hydrogen the catalyst was filtered off, the solvent evaporated and the residue column chromatographed to give **10f** (90%) contaminated by trace amounts of a tetrahydro derivative. **10f**: colorless needles from cyclohexane, mp 114-116 °C; (Anal. Calcd for $C_{21}H_{22}N_2OCl_2$: C, 64.8 ; H, 5.7; N, 7.2. Found: C, 65.0; H, 5.6; N, 7.2.); ^{1}H NMR δ (ppm, $CDCl_3$) 1.47 (m, 4H), 1.69 (m, 4H), 2.01 (m, 2H), 2.27 (s, Me), 2.42 (m, 2H), 6.95-7.35 (m, 7H). ^{13}C NMR δ (ppm, $CDCl_3$) 20.9 (q, Me), 21.5 (t, CH_2), 29.1 (t, CH_2), 38.8 (t, CH_2), 104.5 (s, C-5), 127.9, 128.5, 129.4 and 131.3 (four d, aromatic CH), 126.7, 135.4 and 136.0 and 137.5 (four s, quaternary aromatic carbons), 151.0 (s, C-3).

Hydrolysis of compounds (3f/4f) in acetic acid and methanol. Compounds (**3f/4f**) (200 mg, 0.52 mmol) was dissolved in acetic acid (10 mL) and left aside at rt. 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 ether. TLC analysis showed the presence of tropone and of amidoxime (**9f**) as the only important products. Amidoxime (**9f**) was isolated in 80% yields by column chromatography and was identical in all respects to the compound obtained (75%) from the reaction of 2,6-dichlorobenzonitrile oxide and *p*-toluidine.[18] Amidoxime (**9f**) was also isolated in 71% yield from a solution of 100 mg of **9f** in methanol (15 mL, which obviously contained some water) kept at 35 °C for 3 d.

9f: colorless prisms from benzene, mp ≈ 201 °C (decomp) (Anal. Calcd for $C_{14}H_{12}N_2OCl_2$: C, 57.0 ; H, 4.1; N, 9.5. Found: C, 57.3; H, 3.9; N, 9.6.). IR (Nujol): ν_{max} 3410 (sharp, NH) and 3100 (b, OH) cm^{-1}.

Thermal decomposition of compounds (3/4). A solution of **3f/4f** (200 mg, 0.52 mmol) in toluene (10 mL) was heated at reflux in the presence of 60 mg (0.55 mmol) of *p*-toluidine until TLC analysis showed the disappearance of **3f/4f**. Cooling the solution led to precipitation of bis(*p*-tolyl)urea (28mg, mp 261-263 °C) in 22% yield. A solution of **3g/4g** (100 mg) in anhydrous benzene (5 mL) was kept at 35 °C for 20 d until disappearance of the starting product. IR analysis of the residue from evaporation of the solvent showed two strong absorptions at 2215 (CN) and 2270 (NCO) cm^{-1}. In a duplicate experiment the

reaction mixture after 20 d was treated with *p*-toluidine to afford bis(*p*-tolyl)urea in 78% yield. Decomposition of **3g/4g** was also monitored with ^{1}H NMR in $CDCl_3$, C_6D_6 and CD_3CN. The reaction rate was similar in all the three solvents and after 6 d at 21 °C conversion had reached ≈ 50%. After 45 d the only signals present in $CDCl_3$, were the followings: 2.31 (s, *p*-Me of mesitonitrile and *p*-tolyl isocyanate), 2.48 (s, two *o*-Me of mesitonitrile), 2.91 (br s, 2H, aromatic protons of mesitonitrile), 6.96 and 7.09 (AA'XX' system of the *p*-tolyl group), 7.35 (C_6H_6).

Oxidation of compounds (15) with trimethylamine-*N*-oxide. Compounds (**15f**), (**15g**) and (**15h**)[3] (0.5 mmol), respectively, were dissolved in acetonitrile (10 mL) and excess trimethylamine-*N*-oxide-2H_2O (5 mmol) was added. A strong odor of trimethylamine developed at once and after 15 min TLC analysis showed that compound (**15**) had disappeared while a new yellow spot was present at R_f lower than those of **13** and **17**. The new compound disappeared slowly with time while there was a parallel and progressive increase in intensity of an orange-yellow spot (i.e., **17**). After 10 d the reaction mixture was diluted with ether and washed with water. The residue, left after evaporation of the solvent of the dried organic layer, was column chromatographed to give pure **17f** (65%), **17g** (61%) and **17h** (60%).

17f: orange red prisms from cyclohexane-petrol-ether, mp 165-168 °C. (Anal. Calcd for $C_{21}H_{14}N_2OCl_2$: C, 66.2; H, 3.7; N, 7.4. Found: C, 66.4; H, 3.9; N, 7.4.). ^{1}H NMR δ (ppm, $CDCl_3$) 2.26 (s, Me), 6.36 (ddd, H-6, $J_{5,6}$ = 12.9 Hz, $J_{6,7}$ = 8.0 Hz, $J_{6,8}$ = 1.0 Hz), 6.46 and 7.04 (AA'XX' system of the *p*-tolyl group), 6.55 (ddd, H-7, $J_{5,7}$ = 0.5 Hz, $J_{6,7}$ = 8.0 Hz, $J_{7,8}$ = 11.5 Hz), 6.73 (ddd, H-5, $J_{5,6}$ = 12.9 Hz, $J_{5,7}$ = 0.5 Hz, $J_{5,8}$ = 1.0 Hz), 7.06 (ddd, H-8, $J_{6,8}$ = 1.0 Hz, $J_{7,8}$ = 11.5 Hz, $J_{5,8}$ = 1.0 Hz), 7.25 (m, 1 H, aromatic proton), 7.35 (m, 2 H, aromatic protons); ^{13}C NMR δ (ppm, $CDCl_3$) 20.7 (q, Me), 120.7 (d, C-8), 129.8 (d, C-6), 130.4 (d, C-7), 131.5 (d, C-5), 119.2 and 129.5 (two d, CH of the *p*-tolyl group), 130. 2 and 127.3 (two d, CH of the of the 2,6-$Cl_2C_6H_3$ group), 121.3, 129.0, 132.6, 135.0, 147.1, 152.0, 158.8 and 166.7, (singlets, quaternary carbons).

17g: orange red prisms from petrol-ether, mp 126-128 °C. (Anal. Calcd for $C_{24}H_{22}N_2O$: C, 81.3; H, 6.3; N, 7.9. Found: C, 81.2; H, 6.1; N, 8.2.). ^{1}H NMR δ (ppm, $CDCl_3$) 2.09 (s, two Me), 2.25 and 2.28 (two s, Me), 6.31 (ddd, H-6, $J_{5,6}$ = 12.5 Hz, $J_{6,7}$ = 8.0 Hz, $J_{6,8}$ = 1.0 Hz), 6.38 and 6.99 (AA'XX' system of the p-tolyl group), 6.51 (ddd, H-7, $J_{5,7}$ = 0.8 Hz, $J_{6,7}$ = 8.0 Hz, $J_{7,8}$ = 11.5 Hz), 6.68 (ddd, H-5, $J_{5,6}$ = 12.5 Hz, $J_{5,7}$ = 0.8 Hz, $J_{5,8}$ = 1.0 Hz), 6.83 (br s, 2 H, aromatic protons), 7.02 (ddd, H-8, $J_{5,8}$ = 1.0 Hz, $J_{6,8}$ = 1.0 Hz, $J_{7,8}$ = 11.5 Hz).

17h: orange red glassy solid; (Anal. Calcd for $C_{24}H_{20}N_2OCl_2$: C, 68.1; H, 4.8; N, 6.6. Found: C, 67.9; H, 4.7; N, 6.6.); ^{1}H NMR δ (ppm, $CDCl_3$) 2.16 (s, two Me), 2.18 and 2.51 (two s, Me), 6.32 (ddd, H-6, $J_{5,6}$ = 12.8 Hz, $J_{6,7}$ = 8.0 Hz, $J_{6,8}$ = 1.0 Hz), 6.35 and 7.03 (AA'XX' system of the *p*-tolyl group), 6.54

(ddd, H-7, $J_{5,7}$ = 0.5 Hz, $J_{6,7}$ = 8.0 Hz, $J_{7,8}$ = 11.5 Hz), 6.70 (ddd, H-5, $J_{5,6}$ = 12.8, Hz, $J_{5,7}$ = 0.5 Hz, $J_{5,8}$ = 0.6 Hz), 7.05 (ddd, H-8, $J_{5,8}$ = 0.6 Hz, $J_{6,8}$ = 1.0 Hz, $J_{7,8}$ = 11.5 Hz).

In an alternative protocol the oxidation mixture after 15-30 min at ≈ 21 °C was diluted with carbon tetrachloride, filtered and washed with water. The organic layer was dried with anhydrous sodium sulfate, the solvent evaporated and compounds (**13**) (+ small amounts of **14**) (≈ 40% yields) were separated by a fast column chromatography (benzene as eluant) from variable small amounts of **17**.

In a further experiment to a solution of compound (**15f**) (0.10 mmol) in acetonitrile (1 mL) an excess (0.50 mmol) of trimethylamine-*N*-oxide was added. After 15 min the reaction mixture was cooled to 0 °C and the precipitated orange yellow crystals filtered off, washed with water and then with a small amount of cold acetonitrile. Using deuteroacetonitrile afforded a complex with an IR spectrum which was very similar to that obtained in acetonitrile. In particular, no absorption for CD bond was detectable in this spectrum. Elemental analysis was more consistent with structure (**16f**) with L = MeCN (Anal. Calcd for $C_{25}H_{19}N_3O_3Cl_2Fe$: C, 56.1; H, 3.6; N, 7.85. Found: C, 55.7; H, 3.55; N, 8.0. For the complex prepared in deuteroacetonitrile: Anal. Calcd for $C_{25}H_{16}N_3O_3Cl_2D_3Fe$: C, 55.7; H, 3.6; N, 7.8. Found: C, 55.2; H, 3.5; N, 7.9) than with **16f** with L = Me_3N (i.e., the complex with trimethylamine as ligand, $C_{26}H_{25}N_3O_3Cl_2Fe$, would have required: C, 56.3; H, 4.55; N, 7.6). Saturating the solution of the oxidation reaction with trimethylamine did not produce a different complex.

Decomplexation reaction of $Fe(CO)_5$. Complexes (**22**) and (**24**) (the latter was obtained only in solution by irradiating $Fe(CO)_5$ in hexane in the presence of acetonitrile or in pure acetonitrile) were prepared according to literature procedures.[10,12,14] They exhibited different behavior on TLC (cyclohexane/ethyl acetate = 70:30 as eluant): the former complex showed higher R_f (its spot was orange-red) than the latter one (whose spot was yellow).

A solution of $Fe(CO)_5$ in degassed acetonitrile was treated with trimethylamine-*N*-oxide while bubbling a stream of argon at 0 °C. The reaction was fast and TLC analysis after 15 min showed formation of complex (**24**) while later complex (**22**) appeared and **22**:**24** ratio progressively increased with time (TLC analysis). When the oxidation reaction was carried out in an acetonitrile solution saturated with trimethylamine comparable amounts of **22** and **24** were formed (as judged by TLC) at the beginning but **24** progressively disappeared paralleling the increase in the quantity of **22**. Transformation of **24** into **22** was observed also when acetonitrile solution of **24** [generated photochemically by irradiatiing $Fe(CO)_5$ in degassed acetonitrile with a high pressure mercury lamp (Pyrex filter)] was saturated with trimethylamine while compound (**24**) could not be detected (TLC) when **22** was dissolved in acetonitrile and left at rt.

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