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SITE SPECIFICITY IN CYCLOADDITIONS OF DIPHENYLNITRILE IMINE WITH 8-SUBSTITUTED-8-AZAHEPTAFULVENES AND TRICARBONYL (8-AZAHEPTAFULVENE) IRON COMPLEXES

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Abstract—The reaction of diphenylnitrile imine with 8-substituted-8-azaheptafulvenes is both site and regiospecific and resulted in a mixture of two [8+4]-adducts in high yield. The mechanism of the reaction was investigated. The [8+4]-adducts underwent easily a reversible thermal 1,7-sigmatropic shift involving an sp^3 nitrogen centre. Diphenylnitrile imine reacted also with tricarbonyl(8-azaheptafulvene)iron complexes to give adducts to the C=N double bond, the degradative oxidation of which with trimethylamine-N-oxide was investigated. The specificity of the cycloadditions is briefly discussed on the basis of a simple perturbation theory approach.

Cyclic polyenes have been used as the most suitable compounds for studying peri, site and regioselectivity in 1,3-dipolar cycloadditions. In previous studies Houk *et al.* and one of us have reported the reaction of diphenylnitrile imine (DPNI) 1 with tropone and evidenced both [4+2]-(predominant) and [6+4]-cycloadditions.[1,2] In the case of [4+2]-reactions attacks of the 1,3-dipole at C_2=C_3 (predominant) and C_6=C_7 double bonds were observed, while the C=O double bond was found to be unreactive.

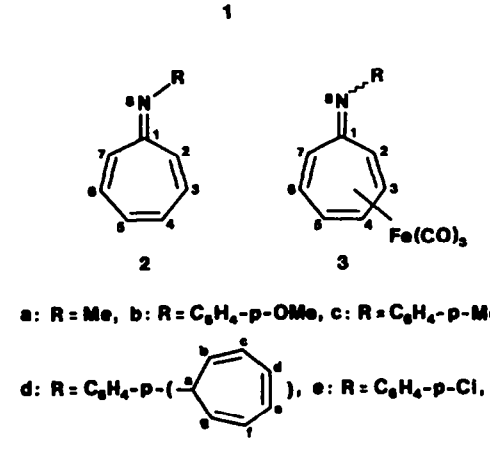
Experiments with tricarbonyltroponeiron as dipolarophile showed that only the free C=C double bond is involved in the 1,3-dipolar cycloaddition with DPNI.[1]

We now report the reactions of 1 with 8-substituted-8-azaheptafulvenes 2 and tricarbonyliron complexes 3. These cyclic polyenes do not appear to have been used as dipolarophiles. However, 8-azaheptafulvenes have been shown to enter other types of pericyclic reactions: they reacted as $_{\pi}8$ electron addends with dimethyl acetylendicarboxylate,[3] ketenes,[4] sulfenes,[5] isocyanates and isothiocyanates[6] to give [8+2]-adducts and with benzoyl isothiocyanate to give an [8+4]-adduct.[6] It was this latter result that led us to believe that 8-azaheptafulvenes could be suitable dipolarophiles for obtaining the hitherto unknown [8+4]-adducts in 1,3-dipolar cycloadditions.

RESULTS AND DISCUSSION

Compounds 2 have been prepared according to the literature.[7,8] The reaction of aniline with tropylium tetrafluoroborate followed by treatment with bases is reported to give 8-phenyl-8-azaheptafulvene.[7] Repetition of this work demonstrated that the claimed 8-phenyl-8-azaheptafulvene is actually compound 2d (Scheme 1) resulting from an electrophilic substitution by tropylium ion both on the amino group and at *para* position of the aromatic ring (Experimental).

Compounds 2 treated with $Fe_2(CO)_9$ in boiling ether afforded mixtures of *E* and *Z* isomers 3 (one isomer prevailed over the other by a factor of 1.5) not yet described in the literature. NMR analysis (Experimental) of complexes 3 did not distinguish between the *E* and *Z*

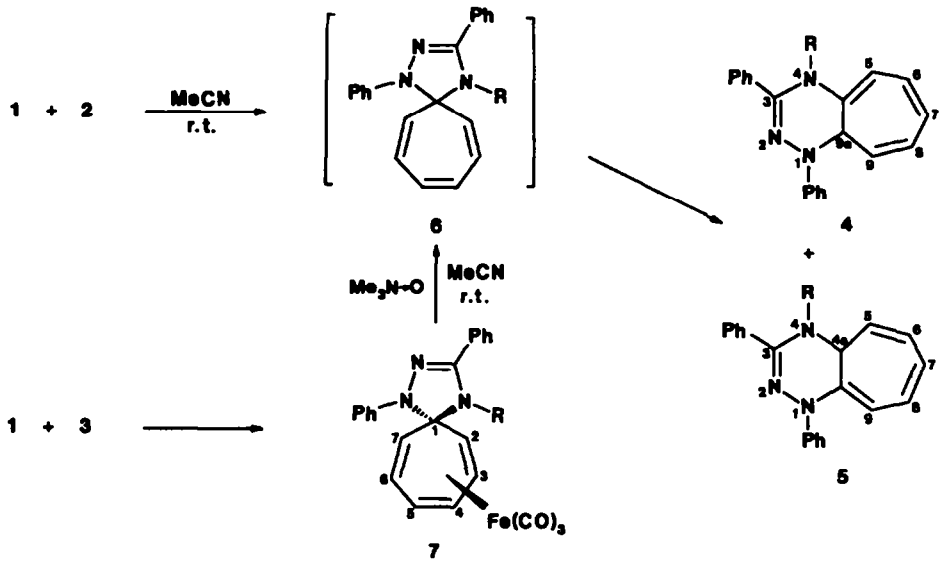


Scheme 1.

Table 1. Comparison of adducts 4 and 5 formation in acetonitrile at 20° (a) from cycloaddition reaction of DPNI 1 with compounds 2 (b) by treatment of adducts 7 with trimethylamine-N-oxide[a]

	Comp.	a	b	c	d	e	f
(a)	4 (%)	100[b]	≥95	≥95	80	65	65
	5 (%)	-	≤5	≤5	20	35	35
(b)	4 (%)	-	70	60	45	10	10
	5 (%)	-	30	40	55	90	90

[a]The results are the mean of two runs.
[b]In C_6H_6.



Scheme 2.

forms but showed that in both compounds the tricarbonyliron group was bonded to an endocyclic diene system.

DPNI 1 reacted readily with equimolar amounts of azaheptafulvenes 2 to give mixtures of variable composition of two [8+4]-adducts 4 and 5 in high yield (Scheme 2 and Table 1). Both compounds 4 and 5 are stable under the reaction conditions. The NMR data of these adducts, the characteristic patterns of which are shown in Table 2, confirm their structures as [8+4]-adducts even though it is not possible to distinguish between the two isomers. However, structures 4 and 5 could be safely attributed on the basis of X-ray analysis of compounds 4e and 5e.[9]

Compound 5a which was not detected in the cycloaddition of 1 with 2a, was obtained quantitatively by dissolving 4a in trifluoroacetic acid and by neutralising subsequently the solution at −10° with triethylamine in acetonitrile (Scheme 3). When transformation 4a→5a was carried out with deuteriotrifluoroacetic acid, no proton-deuterium exchange occurred. The NMR spectra of both 4a and 5a in trifluoroacetic acid were identical and the line patterns showed the presence of two compounds in the ratio 2:1 which are probably two

Table 2. NMR data (δ) of adducts 4a, 5a (C_6D_6) and 4e, 5e ($CDCl_3$)

Comp.	H_5	H_9	H_{4a} or H_{9a}	H_6, H_7, H_8	$J_{4a,5}$ or $J_{9,9a}$ (Hz)
4a[a]	5.27 bd[c]	5.65 dd[d]	3.63 bd	6.18, 6.50 m	6.0
5a[b]	5.40 m	5.92 bd[e]	2.67 bd	6.52 m	6.0
4e	5.40 m	5.95 m	3.60 bd	6.65 m	6.0
5e	5.81 m		2.90 bd	6.65 m	6.0

[a] 2.42 (s, NMe) [b] 2.52 (s, NMe) [c] $J_{5,6}$ = 6.0 Hz

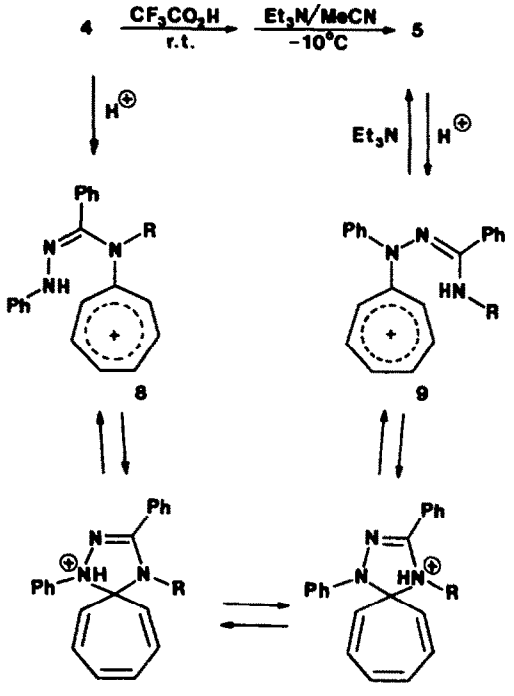
[d] $J_{8,9}$ = 7.8 Hz [e] $J_{8,9}$ = 6.0 Hz

Table 3. Data of the competition reactions of DPNI 1 with excess 2b, norbornene (NB) and 2e, NB[a]

Solvent	E_T[b]	k_{2b}/k_{NB}	k_{2e}/k_{NB}
Acetonitrile	46.0	29.0	11.5
1,2-Dichloroethane	41.9	14.8	5.6
Ethyl acetate	38.1	14.0	7.5
Ethyl ether	34.6	11.7	6.7
Benzene	34.5	14.2	5.7

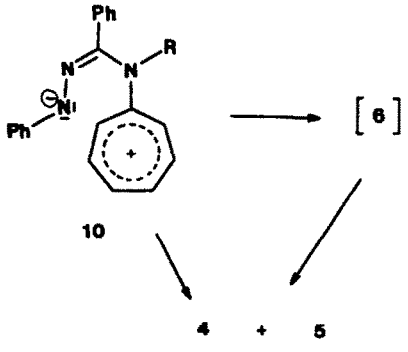
[a] The results are the mean of two runs at 20°.
[b] Parameter of solvent polarity.[19]

stereoisomers of ion 9. This hypothesis was substantiated by the presence of two doublets for the methyls (δ 3.30 and 3.55, collapsing to singlets in CF_3COOD), which coupled with NH proton at δ 9.42 (broad peak, disappearing in CF_3COOD), and of a multiplet for tropylium protons at δ 8.50. We have no explanation for the fact that the equilibrium 8a ⇄ 9a (Scheme 3) is completely shifted towards 9a. The above transformation was also carried out for adducts 4b, c, e and f with similar results.



Scheme 3.

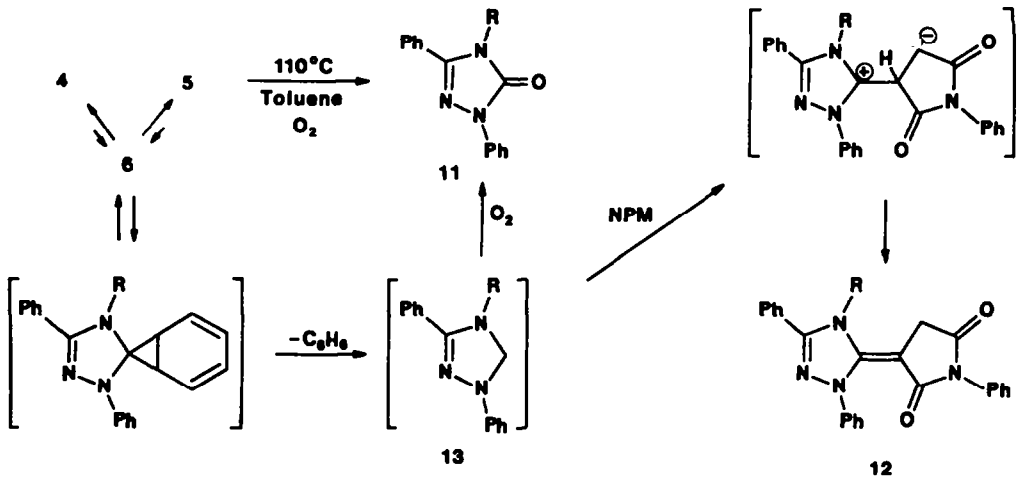
The isolation of compounds 5 in the addition of DPNI to azaheptafulvenes provided good evidence for a reaction via an intermediate [4+2]-adduct 6 which gave rise to the two isomeric triazine derivatives (Scheme 2). Owing to the failure to detect intermediate 6 (e.g. by NMR monitoring of the reaction) we have endeavoured to synthesise 6 by an alternative route. Complexes 3 reacted readily with 1, although more slowly than with azaheptafulvenes 2 [$k_{2a}/k_{3c} = 2.25$ in acetonitrile][a] to give the sole adducts 7. Only one face of the molecule of the dipolarophile is therefore liable to be approached by the 1,3-dipole, probably the side of the complex *anti* to the tricarbonyliron group. The tricarbonyliron group was then easily removed on treatment with trimethylamine-N-oxide[10] to give a mixture of 4 and 5 (both stable under the reaction conditions) in fairly good yield (Scheme 2, Table 1). It is strange at first glance that the ratios 4/5 from such reactions are notably lower than the values obtained in the cycloadditions of 1 and 2. A reasonable explanation lies in the consideration that the cycloaddition reaction involved zwitterion 10 (stabilised by the tropylium ion moiety) which either gives only 4 rapidly or closes to 6 which finally rearranges to 4 and 5 (Scheme 4).



Scheme 4.

In order to substantiate this hypothesis we performed competition reaction experiments. DPNI has been reacted with two couples of dipolarophiles, 2b-norbornene (NB) and 2e-NB respectively, in solvents of different polarity and the results are reported in Table 3. The relative rates (k_{2b}/k_{NB} and k_{2e}/k_{NB}) found demonstrate that the influence of solvent polarity on the reaction rates of 8-azaheptafulvenes with 1 compared with classical concerted 1,3-dipolar cycloadditions[11] involving the same 1,3-dipole (e.g. 1+NB) is too small to support the intermediacy of 10. However the intermediate dipole 10 cannot be definitively discarded if one considers that the charge imbalance arising during the formation of zwitterion 10 enhances the polarity of the transition state whereas the approach of the addends with dipole moments oriented in antiparallel fashion will lower the

[a] Troponetricarbonyliron is about eight times more reactive than tropone itself in benzene.[1]



Scheme 5.

polarity of the transition state in comparison with the polarity of the separate addends. Although the former effect should prevail, it may be partly cancelled out by the second effect thus explaining the small solvent effect observed.[b]

The reactivity and selectivity phenomena found in the foregoing cycloadditions may be to some extent understood in terms of frontier orbital interaction. Theoretical calculations (SCF MO)[12] have shown that HOMO energy of 8-H-8-azaheptafulvene (E = −9.00 eV) is higher than that of tropone (E = −9.47 eV). Moreover it has been reported previously that tropone reaction with DPNI is governed by $HOMO_{tropone} - LUMO_{1,3\ dipole}$ interaction.[1,2] It is therefore quite reasonable that the reactions of 1 with compounds 2 should be governed by the same type of interaction. This hypothesis agrees well with the following experimental data: DPNI is nearly twice as reactive with **2b** than with **2e** (Table 3) and > 50 times (Experimental) more reactive with **2c** than with tropone.

The same MO calculations[12] made available the data of the HOMO coefficients for 8-H-8-azaheptafulvene ($c_1 = -0.094$, $c_2 = 0.38$, $c_3 = 0.23$, $c_4 = -0.34$, $c_8 = -0.59$) and tropone ($c_1 = 0.047$, $c_2 = 0.43$, $c_3 = 0.21$, $c_4 = -0.38$, $c_8 = -0.51$). Thus in the HOMO of both compounds the largest coefficient is on the heteroatom. Moreover, in the HOMO of 8-H-8-azaheptafulvene the coefficients at the heteroatom and at position 2 and 4 are, respectively, larger and smaller than the corresponding ones in tropone.

The carbon atom of DPNI, with the larger LUMO coefficient,[13] should attack preferentially the heteroatom of compounds 2 and of tropone and the site selectivity of the reaction should increase on going from tropone to azaheptafulvenes. The former trend should be lowered and the latter enhanced by the resonance integrals between the interacting centres of the 1,3-dipole and dipolarophiles which increase in the order $\beta_{C-O} < \beta_{C-N} < \beta_{C-C}$.[13]

Theoretical previsions agree well with the results found for the cycloadditions of DPNI with compounds 2 while the complete lack of reactivity of the C=O double bond of tropone with DPNI remains unexplained especially in the light of the strict site specificity observed in the attack at C=N double bond of azaheptafulvenes by the same 1,3-dipole.[c] This latter observation also holds when comparing the reactions of 1 with both tricarbonyltroponeiron and complexes 3 where there is a complete reversal of site specificity. Furthermore, by examining the large differences existing between coefficients at positions 1 and 8, it might be suggested that the attack of the 1,3-dipole to C=N bond of azaheptafulvenes is characterised by a low degree of synchronism suggesting the intermediacy of zwitterion **10**.

A relevant aspect of the reactions studied is the 1,7-sigmatropic rearrangement, involving an sp^3 nitrogen centre, of **6** to **4** and **5** which is, to our knowledge, unprecedented in the literature.[15] A 1,7-process (concerted with inversion at the migrating centre or through a zwitterion intermediate) is in our opinion more probable than two consecutive [1,5]-shifts as the first formed product of the latter mechanism is highly strained (molecular models). The data of Table 1 show that formation of **5** over **4** is favoured by the increasing electron withdrawing power of N-R group. Rearrangement **6** → **4** + **5** is reversible in mild conditions; in boiling tetra hydrofuran both **4b** and **5b** gave mixtures of **4b** + **5b** (ratio **5b**/**4b** = 1.02). An independent proof that interconversion **4b** ⇄ **5b** goes through the intermediate **6b** is provided by the formation of triazolinone **11b** as by product. Compound **11b** is formed in high yield when the reaction is carried out at 110° in the presence of air while compound **12b** is isolated when N-phenylmaleimide (NPM) is added to the reaction mixture (Scheme 5). Also compounds **4e** and **5e** showed a similar thermal behaviour (equilibrium ratio **5e**/**4e** = 3.0). Structures **11**

[b] Two alternative mechanisms may explain the different ratios **4**/**5** found for cycloadditions and oxidative degradation reactions: (i) a competition between a concerted $[_\pi 8_s + _\pi 4_s]$ cycloaddition which give the sole **4** and a concerted $[_\pi 4_s + _\pi 2_s]$ cycloaddition which give **4** and **5** through the intermediate **6** (ii) a contemporaneous 1,7-sigmatropic process with the removal of tricarbonyliron group in the oxidative degradation reaction. Consequently for this reaction the rearrangement could not take place for free **6**.

[c] From selectivity and relative reactivity data of the reactions of tropone and **2c** with DPNI, C=N double bond of azaheptafulvenes is evaluated to be > 10^3 more reactive than C=O double bond of tropone. In the case under scrutiny $k_{C=N}/k_{C=O}$ is at least ten times greater than the value reported for the couple benzylidenemethylamine/benzaldehyde ($k_{C=N}/k_{C=O} = 100$).[14]

were assured by an independent synthesis of 11e from 1 and *p*-chlorophenylisocyanate;[16] structures 12 were assigned on the basis of spectroscopic data (Experimental). The formation of compounds 11 and 12 is consistent only with the presence of the nucleophilic carbene 13.[17] Compound 4a was converted into 11a on heating in benzene, while 5a was found to be stable even at 140° in xylene as a result of the scarce tendency of NMe group to undergo 1,7-sigmatropic rearrangement.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were obtained as Nujol suspensions on a Perkin Elmer 257 spectrophotometer. The NMR spectra (60 MHz) were recorded at 36° on a Perkin Elmer R12 spectrometer with TMS [hexamethyldisiloxane (≃0.1 δ from TMS) for 4a and 2d · HBF_4] as internal standard by Dr. A. Gamba Invernizzi. Microanalyses were performed by Dr. L. Maggi Dacrema. Satisfactory analytical data (±0.4% for C, H and N) were obtained for all new compounds. Column chromatography separations and tlc analyses were performed with silicagel 60 (70-230 mesh) and GF_{254} (Merck), respectively, eluting with cyclohexane/AcOEt and cyclohexane/benzene mixtures in various proportions. The identification of samples from different experiments was secured by mixed m.ps and by comparison of IR and NMR spectra and R_F values (tlc). The spectral data of compounds in the series b–e were very similar therefore only the data of one compound for each series are reported. The claim of specificity for a reaction was based on NMR and tlc analyses of the crude product.

Synthesis of azaheptafulvene 2d. Aniline (40.0 mmol) was added dropwise to a suspension of tropylium tetrafluoroborate (40.0 mmol) in water (40 ml) at ice bath temp during a period of 1 hr with vigorous stirring. The mixture was left aside for 24 hr and, during this time, the viscous oil formed slowly crystallised. The solid was then collected by filtration, washed with benzene several times and recrystallised twice from isopropyl alcohol to give pure 2d · HBF_4 [30%, m.p. 143–145° (lit.[7] 147°); δ (DMSO-d_6) 2.75 (1H, bt, H_a, J = 5.4 Hz), 5.37 (2H, dd, H_b and H_g, J = 5.4 and 9.0 Hz), 6.3 (2H, m, H_c and H_f), 6.73 (2H, m, H_d and H_e), 7.52 (4H, AA'BB' system, aromatic protons), 7.80 (6H, m, H_7–H_7)].

To a stirred suspension of 2d · HBF_4 in dry ether an excess of triethylamine was added. After 30 min the orange mixture was washed with water, dried and the solvent evaporated to give an almost quantitative yield of 2d [m.p. 89–90° (lit.[7] 90–91°)]

Synthesis of tricarbonyl(8-aryl-8-azaheptafulvene)iron complexes 3. A slurry of azaheptafulvenes 2 (4.0 mmol) and diiron enneacarbonyl (8.0 mmol) in dry ether (50 ml) was refluxed in the absence of air under N_2 for 5 hr and then left overnight. Filtration of the mixture and evaporation of the solvent afforded an oily residue which crystallised from petrol ether to give pure 3c (63%), 3d (75%), 3e (70%) and 3f (74%), in the yields indicated. Compound 3b (50%) was purified by column chromatography. 3e: ν_{max}, 2070 and 1990 (coordinated CO) cm^{-1}; major isomer, δ ($CDCl_3$) 2.75 (m, H_3), 3.72 (m, H_2), 5.15 (m, H_7), 6.56 (4H, AA'BB' system, aromatic protons); minor isomer, δ 2.90 (m, H_3), 3.24 (m, H_2), 5.45 (m, H_7), 6.95 (4H, AA'BB' system, aromatic protons); H_3, H_4 and H_6 of the two isomers resonated at very similar field values and gave a complex signal at δ 5.70–6.40.

An attempt to prepare 3a failed.

Reaction of DPNI with azaheptafulvenes. A soln of 2 (5.0 mmol), N-α-chlorobenzylidene-N'-phenylhydrazine (5.0 mmol) and triethylamine (15.0 mmol) in acetonitrile (50 ml) was left at room temp and stirred for 5 hr. The mixture was then diluted with CH_2Cl_2, washed with water and dried. The solvent was evaporated *in vacuo* and the residue analysed by NMR to obtain 4/5 in the ratios reported in Table 1. Overall yields (>90%) of 4+5 were determined by column chromatography on silicagel. Compounds 4b, 4c, 4e and 4f were obtained in a pure state by fractional crystallisation of the crude product from methanol-AcOEt. We were not able to separate 4d and 5d.

Reaction rates and the ratios 4/5 were found to be solvent dependent: the reaction rate decreased in the order acetonitrile > 1,2-dichloroethane > AcOEt > benzene > ethyl ether and the ratio 4e/5e fall down from 1.9 in acetonitrile to ≃1.0 in benzene, 1,2-dichloroethane and AcOEt.

Isomerisation of adducts 4 *to adducts* 5. To a soln of triethylamine (2 ml) in acetonitrile (10 ml) a soln of 4 (a, b, c, e and f) in trifluoroacetic acid (1 ml) was added dropwise at −10° under vigorous stirring. The mixture was diluted with CH_2Cl_2, washed with water, dried and evaporated to give quantitatively 5 (a, b, c, e and f).

The NMR spectra of compounds 4 and 5 in trifluoroacetic acid are superimposable, e.g. 4b and 5b, δ (CF_3CO_2H) 3.84 and 3.98 (3H, two singlets, OMe, ratio 2.5:1), 6.90–8.00 (14 H, complex, aromatic protons), 8.5 (6 H, m, tropylium ion moiety protons).

Competition reactions of DPNI

(a) *with NB + 2b and with NB + 2e.* A soln of N-α-chlorobenzylidene-N'-phenylhydrazine (1.0 mmol), norbornene (6.0 mmol), 2b or 2e (2.0 mmol) and triethylamine (3.0 mmol) in the appropriate dry solvent was left in the dark at 20 ± 1° until tlc analysis showed the disappearance of α-chlorobenzylidenephenylhydrazine. The mixture was diluted with CH_2Cl_2, washed with water and dried. After evaporation of the solvent column chromatography of the residue gave a quantitative yield of adducts DPNI-NB, 4 and 5. The ratios DPNI-NB/4b + 5b were determined by column chromatography; the ratios DPNI-NB/4e + 5e both by NMR and column chromatography. The evaluation of the results were carried out according to Huisgen *et al.*[19]

(b) *With tropone and* 2c. A soln of N-α-chlorobenzylidene-N'-phenylhydrazine (1.0 mmol), tropone (4.85 mmol), 2c (1.16 mmol) and triethylamine (3.0 mmol) in dry benzene (20 ml) was allowed to stand in the dark at 20° ± 1 for 48 hr. After usual work up column chromatography of the residue afforded 93% of 4c + 5c and 5% of 1,3-diphenylcycloheptapyrazol-4 (1H) one (aromatised adduct of DPNI to tropone). The ratio $k_{2c}/k_{tropone} = 57.5$ was evaluated estimating a 7% yield for tropone adducts as the minor products contaminating the principal one[1] were not isolated.

(c) *With* 2c *and* 3c. The competition reaction was carried out in dry acetonitrile operating as above with a ratio DPNI/2c/3c = 1.0/1.5/1.5. Column chromatography afforded 64.5% of 4c + 5c and 30.5% of 7c.

Reaction of DPNI with complexes 3 *and oxidative degradation of adducts* 7.

A soln of complexes 3 (5.0 mmol), N-α-chlorobenzylidene-N'-phenylhydrazine (5.0 mmol) and triethylamine (15.0 mmol) in acetonitrile was stirred at room temp for 6 hr. After the usual work up column chromatography of the residue afforded pure 7 (b – f) in >80% yields. 7e: ν_{max} 2060, 2020 and 1985 (coordinated CO) cm^{-1}; δ ($CDCl_3$) 2.75 (1H, bt, H_5, $J_{5,6}$ and $J_{4,5}$ = 8.0 Hz), 3.05 (1H, dd, H_2, $J_{2,3}$ = 8.0 Hz and $J_{2,7}$ = 3.0 Hz), 4.80 – 5.35 (2H, m, H_3 and H_4), 5.53 (1H, dd, H_7, $J_{6,7}$ = 11.0 Hz), 6.20 (1H, dd, H_6).

A suspension of 7 (1.0 mmol) and trimethylamine-N-oxide (8.0 mmol) in acetonitrile was left at room temp for 12 hr. The mixture was then diluted with CH_2Cl_2, filtered, washed with water and dried. The analysis showed the presence of adducts 4 and 5, small amounts of compounds 11 and trace amounts of other products not identified. Evaporation of the solvent gave a residue which was chromatographed on a short basic alumina column to give mixtures 4 + 5 (b, 58%; c, 55%; d, 61%, e, 50%; f, 69%) whose ratios were determined by NMR. From the reaction of 7b compound 11b was isolated in 8% yield.

Thermal behaviour of compounds 4 *and* 5.

(a) A soln of 4b or 5b (0.5 mmol) in THF (30 ml) was refluxed under N_2 for 30 hr. After evaporation of the solvent, column chromatography through a short basic alumina column afforded (in order of elution) 4b + 5b [≃50%, ratio 4b/5b (NMR) = 45/55] and 11b (≃17%). Operating as above a mixture 4e + 5e [≃65%, ratio 4e/5e = 25/75] and 11e (≃6%) were isolated from 4e or 5e.

(b) Adducts 4e and 5e were separately dissolved in dry toluene (15 ml) and refluxed for 2.5 hr. The solvent was evaporated to give a solid residue the IR spectrum of which was identical with that of 11e.

The triazolinone 11e (ν_{max} 1715 (C=O) cm^{-1}) was also syn-

Table 4. Physical data of compounds 3, 4, 5, 7, 11 and 12[a]

Comp.	M.p. °C	Recryst. solv.	Comp.	M.p. °C	Recryst. solv.
3c	96–98	Petrol ether[b, c]	5e	147	AcOEt[d, e]
3d	112–113	Cyclohexane[b, c]	5f	155–156	Methanol[b, d]
3e	109–111	Petrol ether[b, c]	7b	129–131	Cyclohexane[b, c]
3f	119–121	Petrol ether[b, c]	7c	123–125	Petrol ether[b, c]
4a	123–124	Cyclohexane[b, d]	7d	161–162	Acetonitrile[b, d]
4b	162	AcOEt[b, d]	7e	135–138	Acetonitrile[b, c]
4c	167	AcOEt[b, d]	7f	159–160	Acetonitrile[b, c]
4e	148	AcOEt[b, d]	11e	113–114	Cyclohexane[e]
4f	153–155	AcOEt[b, d]	11b	229–232	Methanol[e]
5a	93–95	Petrol ether[d, e]	11e	204–207	Methanol[e]
5b	142–144	Acetonitrile[d, e]	12b	237–240	Benzene[e]
5c	167	AcOEt[d, e]	12e	245–248	Benzene[e]

[a] Compounds 4, 5 and 7 melted with decomposition
[b] Prisms [c] Orange [d] Yellow [e] Needles

thesised by heating a mixture of 2,5-diphenyltetrazole (1.0 g) and of *p*-chlorophenyl-isocyanate (4.0 g) in the presence of small amount of basic alumina at 160° under N_2 for 4 hr. The mixture solidified and after cooling at room temp was triturated and poured into a water (15 ml)/benzene (30 ml) mixture. The benzene layer was separated, filtered, dried and the solvent evaporated *in vacuo*. Crystallisation of the residue from MeOH afforded 0.4 g of 11e.

Thermolysis of 4b and 5b gave similarly quantitative yields of 11b (ν_{max} 1705 (CO) cm^{-1}.

Thermolysis of 4a (300 mg) was carried out in boiling benzene for 30 hr. The triazolinone 11a (180 mg, 74%) was purified by

Table 5. Analytical data of compounds 2d, 3, 4, 5, 7, 11 and 12

	Found %				Calc. %		
Comp.	C	H	N	Formula	C	H	N
2d	88.3	6.4	5.3	$C_{20}H_{17}N$	88.5	6.3	5.2
3c	60.8	3.7	4.0	$C_{17}H_{13}FeNO_3$	60.9	3.9	4.2
3d	67.5	4.3	3.6	$C_{23}H_{17}FeNO_3$	67.2	4.2	3.4
3e	54.4	2.9	3.7	$C_{16}H_{10}ClFeNO_3$	54.0	2.8	3.9
3f	48.4	2.5	3.4	$C_{16}H_{10}BrFeNO_3$	48.0	2.5	3.5
4a	80.6	6.2	13.4	$C_{21}H_{19}N_3$	80.5	6.1	13.4
5a	80.2	6.3	13.2				
4b	79.8	5.7	10.5	$C_{27}H_{23}N_3O$	80.0	5.7	10.4
5b	80.2	5.5	10.3				
4c	83.1	5.8	10.4	$C_{27}H_{23}N_3$	83.3	5.9	10.8
5c	83.0	5.6	10.9				
4e	76.5	5.3	10.0	$C_{26}H_{20}ClN_3$	76.2	4.9	10.3
5e	76.6	5.2	10.1				
4f	68.5	4.2	9.1	$C_{26}H_{20}BrN_3$	68.7	4.4	9.2
5f	68.9	4.1	9.3				
7b	66.4	4.3	7.5	$C_{30}H_{23}FeN_3O_4$	66.1	4.2	7.7
7c	68.2	4.5	7.6	$C_{30}H_{23}FeN_3O_3$	68.1	4.4	7.9
7d	71.8	4.7	6.7	$C_{36}H_{27}FeN_3O_3$	71.4	4.5	6.9
7e	63.0	3.9	7.7	$C_{29}H_{20}ClFeN_3O_3$	63.3	3.7	7.6
7f	58.5	3.5	7.5	$C_{29}H_{20}BrFeN_3O_3$	58.8	3.4	7.1
11a	72.1	5.4	16.9	$C_{15}H_{13}N_3O_3$	71.7	5.2	16.7
11b	73.6	4.8	12.2	$C_{22}H_{17}N_3O_2$	73.4	5.0	12.2
11e	69.4	4.1	11.6	$C_{20}H_{14}ClN_3O$	69.1	4.1	12.1
12b	74.7	5.1	11.6	$C_{31}H_{24}N_4O_3$	74.4	4.8	11.2
12e	71.6	4.3	11.4	$C_{30}H_{21}ClN_4O_3$	71.4	4.3	11.1

column chromatography. **11a**: ν_{max}, 1705 (C=O) cm^{-1}; δ ($CDCl_3$) 3.43 (3H, s, Me), 7.20–8.40 (10H, complex, aromatic protons).

(c) A soln of **4b** (1.0 mmol) and NPM (1.0 mmol) was heated in a sealed ampoule at 110° for 2 hr. The mixture was then cooled to room temp and the precipitated **12b** (0.380 g, 76%) collected by filtration. **12b**: ν_{max}, 1725 and 1675 cm^{-1}; δ ($CDCl_3$) 2.75 (2H, s, CH_2), 2.85 (3H, s, OMe), 6.90–7.80 (19H, complex, aromatic protons).

The thermolysis of **4e** in the presence of NPM gave **12e** (50%) and **11e** (11%). Similar results (25% of **12e** and 36% of **11e**) were obtained carrying out thermolysis at 110°c, then bringing the temp down to 20° and adding NPM. This result suggest that **13** is not distinguishable from its dimer on the basis of reactivity; this behaviour is well documented for other nucleophilic carbenes.[17]

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