Tetrahedron Vol. 42, No. 3, pp. 923 to 936, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00

SITE SELECTIVITY IN THE REACTION OF TETRACYANOETHENE WITH TETRACYCLO [5.3.2.$0^{2,10}$. $0^{3,6}$] DODECA-4,8,11-TRIENE. A BORDERLINE CASE OF HOMO-DIELS-ALDER REACTION.

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(*Received in UK 7 November* 1985)

Abstract - Tetracyanoethene reacted with tetracyclo [5.3.2.$0^{2,10}$.$0^{3,6}$] dodeca-4,8,11-triene (**1**) according to two competitive reaction modes, both involving the sole homotropilidene moiety, to give a mixture of adducts **4** and **6**. Structure **6** was established by X-ray analysis. Compounds **4** and **6** result from a thermally allowed homocycloaddition and a forbidden [π^2_s + σ^2_s + π^2_s + π^2_s] reaction, respectively. The reaction rate and the **6**:**4** ratio increased on passing from benzene to nitromethane as reaction medium. The homo-Dies-Alder reaction leading to **4** was shown to be reversible. In methanol compound **4** gave rise to a zwitterion which was trapped by solvent. Reaction mechanisms are discussed. A zwitterion is proposed as intermediate on the pathway to **6** whereas experimental findings do not permit a definitive choice between an ionic two step and a concerted cycloaddition in the formation of **4**. The neutral and base catalyzed addition of methanol to the tetracyanoethylene moiety of **4**, **6** and related derivatives was also investigated.

INTRODUCTION

Tetracyanoethene (TCNE) and N-substituted triazolindiones (TAD) are uniparticulate electrophiles whose cycloadditions exhibit a marked dipolar character. Recent studies[1,2] on reactions of TCNE or TAD with polycyclic polyenes, containing both a strained double bond and a homodiene moiety, have revealed that in some instances dipolar cycloaddition at the double bond favourably competes with homo-Diels-Alder cycloaddition. Thus, in acetone PTAD attacks the cyclobutene system of tricyclo [4.2.2.$0^{2,5}$] deca-3,7,9-triene (Nenitzescu hydrocarbon) 2.3 times faster than the homodiene moiety of the same molecule.[1a] Moreover in benzene the exo dipolar attack by TCNE on the norbornene like double bond of bicyclo [3.2.1] octa-2,6-diene occurs five times faster than endo attack resulting in a homocycloaddition.[2]

Tetracyclo [5.3.2.$0^{2,10}$.$0^{3,6}$] dodeca-4,8,11-triene (**1**) (Scheme 1) contains both a strained cyclobutene moiety and a homotropilidene system whose proclivity to enter homodiene cycloaddition is well documented.[3-6] Consequently it seems an ideal model to further explore the competitive nature of the aforementioned diverse reaction modes of strong uniparticulate electrophiles.

A further possibility can be envisaged for the reaction of **1** with TCNE, that is an elec-

trophilic attack at position 8 (or 12) to give the zwitterion5.This intermediate may subsequently ring close to give: i) the product of a formal $[\pi^2_s + \sigma^2_s + \pi^2_s + \pi^2_s]$ thermally forbidden cycloaddition, i.e. **6**; ii) a cyclobutane derivative, i.e. **7**; and iii) the product of a thermally allowed $[\pi^2_s + \sigma^2_s + \pi^2_s]$ cycloaddition to the vinylcyclopropane system of **1**, i.e. **8**. The latter process can obviously occur in a concerted manner as it has been elegantly established for the reaction of TCNE with benzvalene[7a] and with homofuran and homothiophene.[7b] The first reaction type has been already reported for the reaction of MTAD with semibullvalene[8] as well as for the reaction of MTAD, PTAD and TCNE with bullvalene[9,10] but it is unprecedented for barbaralane[3,4] and dihydrobullvalene[4] systems. The second one is a well known reaction of TCNE with vinylcyclopropane derivatives.[11]

We report here on the site selectivity in the reaction of **1** with TCNE and on the mechanism of the homo-Diels-Alder reaction leading to **4**.

RESULTS AND DISCUSSION

Compound **1** reacted sluggishly ($\simeq$20 days) with excess TCNE in benzene at room temperature to afford the homodiene adduct **4** (Scheme 1) which precipitated from the reaction mixture as a crystalline product. The structure of **4** rests firmly on analytical and spectral data and on its propensity (see below) to enter a thermal cycloreversion reaction to **1** and TCNE. In particular, the presence of two cyclopropyl residues [$\delta(CDCl_3)$, 1.50(m, 6H)], of an unchanged cyclobutene double bond [δ 6.28(s, 2H)] and of four protons in an allylic or cyclopropylcarbinyl position [δ 3.64(m, 4H)] is safely inferred from ^{1}HNMR of **4**.

A careful analysis of the mother liquors permitted us to detect small amounts of a second adduct, i.e. **6** (Total yield 93%; **4**:**6** = 25). The temperature independent ^{1}HNMR spectrum of this adduct [$\delta(CDCl_3)$, 3.15-3.88 (m, H-1, H-2, H-5, H-6, H-7 and H-10), 5.80 (dd, H-11 and H-14, $J_{11,12}$

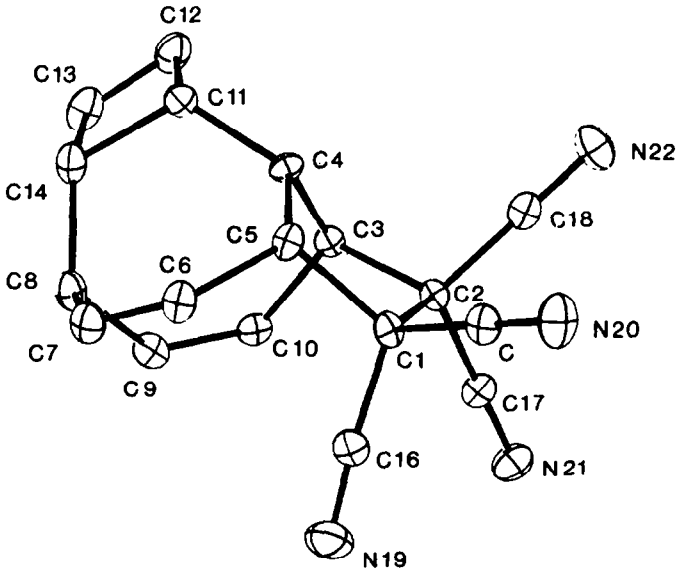
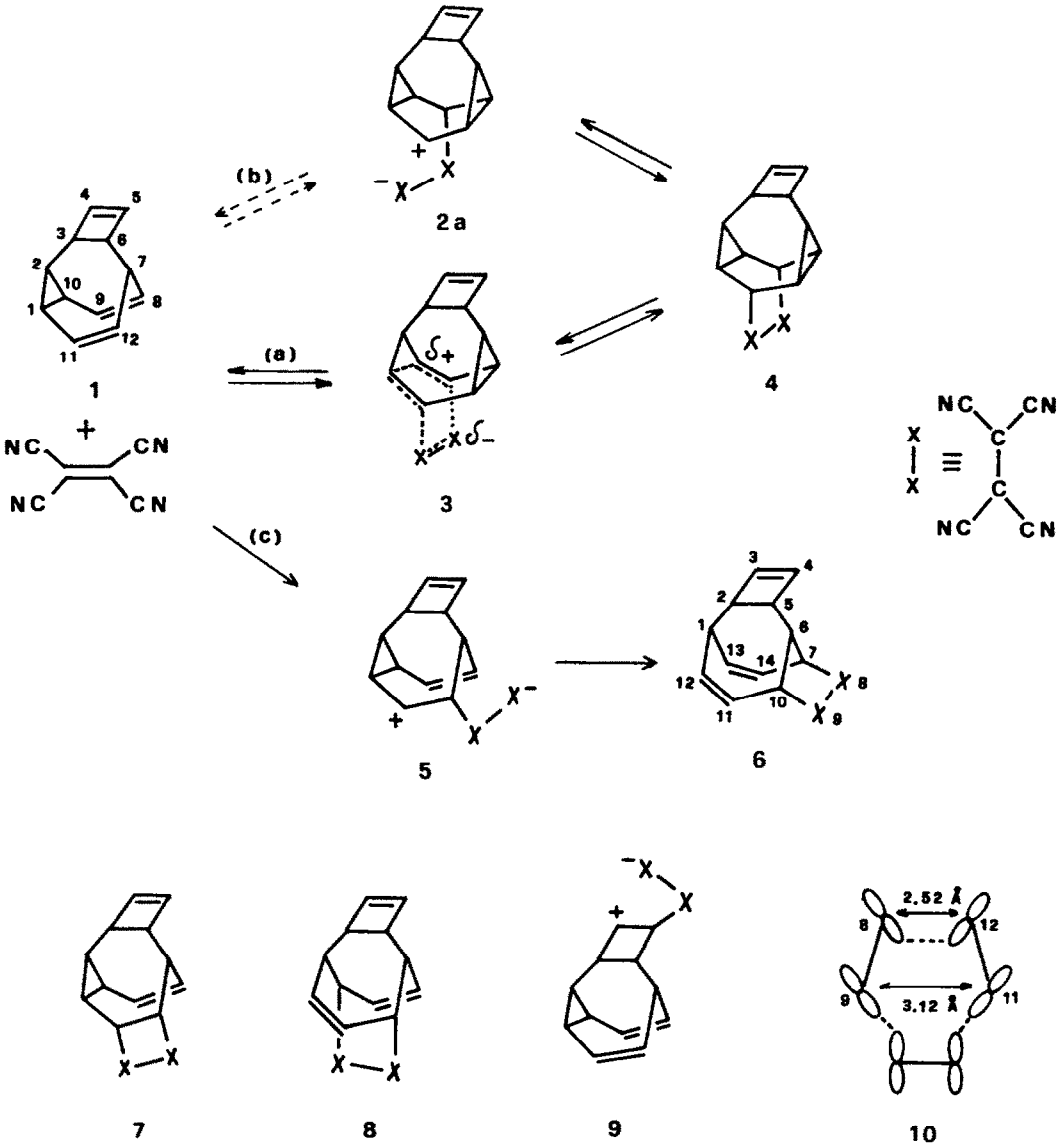


Figure - The crystal structure of **6** showing the atomic numbering used in Tables 1 - 3.

= $J_{13,14}$ = 11.0Hz, $J_{7,14}$ = $J_{10,11}$ = 5.8 Hz), 6.05 and 6.17 (two d, H-3 and H-4, $J_{3,4}$ = 3.0 Hz), 6.22 and 6.55 (two m, H-12 and H-13, $J_{1,12}$ = $J_{1,13}$ = 9.0 Hz)] clearly indicates that it no longer contains a homotropilidene moiety. The cyclobutane structure **7** was excluded by the absence of high field resonances expected for hydrogens on a cyclopropane ring. A single crystal X-ray analysis (Figure) unequivocally confirmed the structural assignement allowing us to eliminate **8** as a possible alternative.

In order to explore the possibility of changing the reaction outcome we decided to study the effect of the polarity of the reaction medium. In fact a relevant solvent effect on product ratios was previously observed by us in the reaction of bullvalene with TCNE.[9] Thus, in nitromethane compound **1** was found to react readily (≃ 24 h) with excess TCNE at room temperature. Also in this



Scheme 1

case the homodiene adduct **4** was dominant but much more substantial amount of **6** was detected so that the **4**:**6** ratio dropped down to 2.3 (Total yield, 69%). We succeeded in reversing the **4**:**6** ratio (**4**:**6** = 45:55) by carrying out the reaction in hexafluoropropanol, a much more polar solvent than nitromethane, but the total yield (38%) was disappointingly low.

Compound **6** was obtained in a pure state (40%) by heating the nitromethane reaction mixture at 90°C during 35 h. Pure **6** could also be prepared (38%) by heating pure **4** in nitromethane in the presence of TCNE. These findings represent good evidence that a reversible homodiene cycloaddition leading to **4** was competing with a slower but irreversible reaction yielding **6**. In fact **6** proved stable under a heating temperature of 90°C in nitromethane or benzene, whereas under the same conditions compound **4** gave **6**, **1** and tarry products.

The presence of a $C_{12}H_{12}^{+\cdot}$ radical ion (base peak) in the mass spectrum of **6** shows that the **6** → **1** + TCNE cycloreversion which does not take place under mild heating, is the dominant fragmentation pathway of **6** under electron impact.

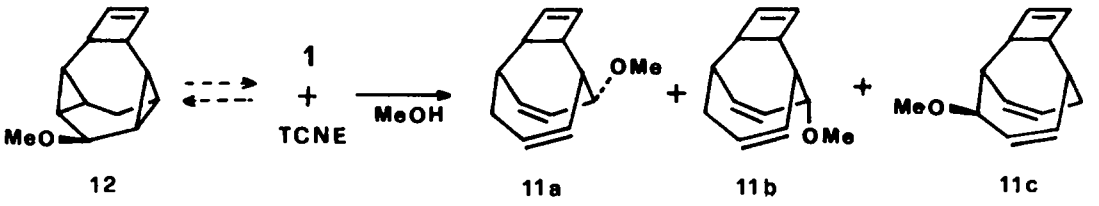
It is worth noting that no products that might have arisen from an attack by TCNE at the cyclobutene moiety of **1** were detected in the reaction mixtures. Therefore, we conclude that the reactivity of a homotropylidene system towards electron deficient dienophiles such as TCNE is higher than that of a strained cyclobutene.

The difference between IP of a cyclobutene system condensed to a carbocyclic moiety (IP_v = 9.42)[12] and that of an ethano-bridged homotropylidene system (IP_v = 8.32)[13] as well as the stability of the possible intermediate zwitterions **2** and **5**[14,15] higher than that of **9** can, both, be advanced as a reasonable explanation of the site selectivity found. In particular the cationic centre in **2** is highly stabilized by two cyclopropyl moieties locked in the required bisected conformation.[16] In fact a properly oriented cyclopropyl group is more effective at stabilizing a cationic centre than a double bond or a phenyl substituent.[17] On the other hand the geometrical array of atoms and orbitals of compound **1** (i.e. **10**) is similar to that recently suggested as a very favourable one for concerted homodiene cycloadditions.[18,19] Consequently the question arises whether we are dealing with a two step or concerted homo-Diels-Alder reaction. The qualitative data cited above show that the reaction rate enhancement on passing from benzene to nitromethane is far from being dramatic:[20] a tenfold increase in rate can, roughly, be evaluated for the formation of **4**. Moreover product ratio values indicate that the formation of **6** is accelerated at least ten times more than that of **4**. In our opinion, these findings clearly support the intermediacy of **5** [path(c), Scheme 1] on the pathway to **6** and slightly favour a concerted though not synchronous cycloaddition *via* a polar transition state [i.e. **3**, path (a)] over a two-step reaction [i.e. path(b)] on the pathway to **4**.

Solvent effects on product ratios even lower than that found by us has been proposed as consistent with a competition between processes *via* zwitterionic intermediates and concerted reactions: e.g. a 3.5 and 3.0 fold variation of isomer ratios on passing from benzene and pentane to acetonitrile in the reaction of chlorocyanoacetylene with norbornene[21] and of TCNE with benzvalene,[7a] respectively.

In the hope of discovering something further about the reaction mechanism we tried trapping experiments by carrying out cycloaddition **1** → **4** and cycloreversion **4** → **1** in methanol.

TCNE reacted with methanol faster than with **1**, the reaction mixture became acidic and compounds **11a** - **c** (**a**:**b**:**c** = 4:1:6) arising from acid (or TCNE)[22,23] catalyzed addition of methanol to **1** were isolated. As the ether **12** would be expected not to revert to **1** and MeOH under the reaction condi-

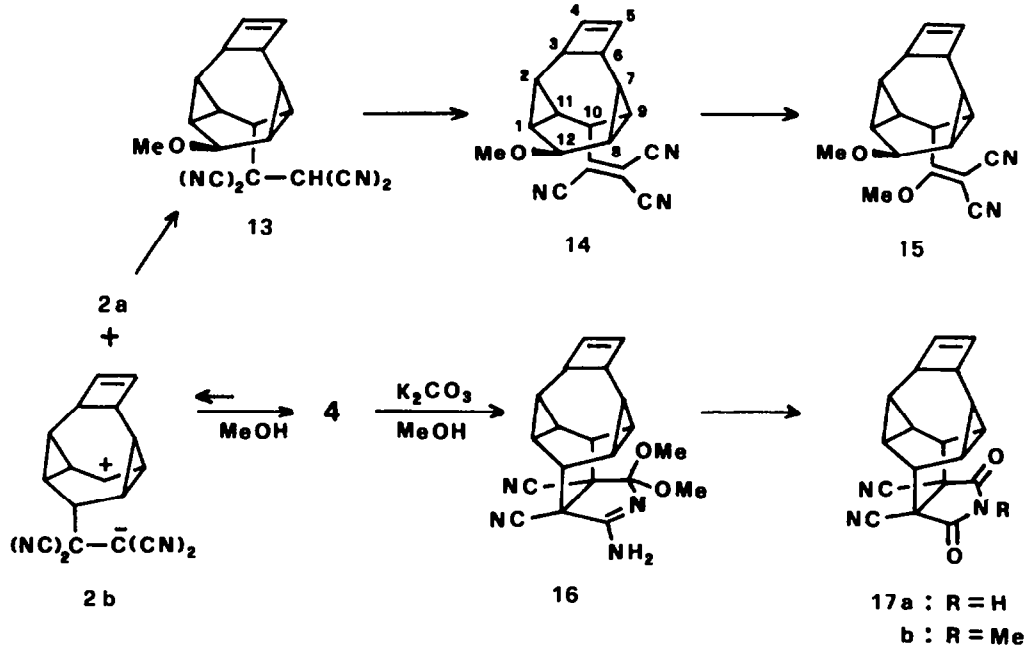


12 11a 11b 11c

tions,[24] this finding indicates that "genuine" two step electrophilic additions to **1** go via carbocations of the type **5** rather than carbocations of the type **2**. The attack of electrophiles at positions 8 or 12 of **1** could also be favoured by the fact that largest HOMO coefficients in a divinylcyclopropane system (by analogy with 1,3,5-hexatriene) are located at the end atoms.

TLC analysis of a solution of **4** in methanol (at 40°C) showed that **4** slowly disappeared (3 days), however without affording neither **1** nor compounds **11**. Four products of the type **13** (**14** upon loss of hydrogen cyanide from **13**) could arise from methanolysis (Scheme 2). Infact outside and inside attacks by solvent on dipolar ion **2a** and regioisomer **2b** are "a priori" possible.[20] Column chromatography of the reaction mixture furnished the sole isomer **14** in moderate yields. The precursor of **14**, i.e. **13**, could not be obtained in a pure state but was detected and fully characterized by ^{1}H and $^{13}CNMR$ analysis (see Experimental) of the crude reaction mixture.

The presence of the tricyanovinyl group in **14**, which gives rise to a very weak absorption at 2235 cm^{-1} in the IR spectrum, finds support in the UV spectrum (λ_{max}^{MeOH} 243 nm, log ε = 4.00). Furthermore the position and intensity of the absorption band changed with time as a result of the



Scheme 2

progressive and quantitative replacement of a cyano group by a methoxy group to give **15** [λ_{max}^{MeOH} 255 nm, log ε = 4.15; ν_{max} 2210 (m, CN) cm^{-1}]. Under the high dilution conditions of the UV spectrum the whole process **4** → **13** → **14** → **15** took place spontaneously. In much more concentrated solutions both **13** and **14** proved more stable. For example traces of **15** could, at most, be detected in the methanolysis reaction of **4** described above after ten days and the synthesis of **15** from **14** on a preparative scale required the presence of base.

NMR spectra are fully consistent with the structure of the carbocyclic moiety of **14** [^{13}C NMR: δ ($CDCl_3$) 15.1, 19.15 and 21.0 (three d, C-1, C-2, C-7, C-8, C-9 and C-11), 34.05 (d, C-10) 44.3 (d, C-3 and C-6), 55.2 (q, Me), 73.4 (d, C-12), 139.35 (d, C-4 and C-5), additional singlets of very low internsity at 109.3, 113.0 and 153.95 can be attributed to carbon atoms of the tricyanovinyl moiety; ^{1}HNMR: δ (C_6D_6), 0.24 (t, H-9 and H-11, $J_{1,11} = J_{2,11}$ = 9.0 Hz), 0.78 (m, H-2 and H-7, $J_{1,2}$ = 9.0 Hz and $J_{2,3}$ = 3.0 Hz), 1.10 (dt, H-1 and H-8, $J_{1,12}$ = 6.5 Hz), 3.15 (s, Me), 3.45 (d, H-3 and H-6), 3.56 (s, H-10), 4.38 (t, H-12), 5.84 (s, H-4 and H-5)] in particular with the presence in it of a symmetry plane. Moreover in the ^{1}HNMR spectrum H-10 appears as a singlet whilst H-12 gives rise to a triplet. This is sure proof that H-10 and H-12 bear a different stereochemical relationship with respect to their vicinal cyclopropyl protons as depicted in **14**. Thus an outside attack on the dipolar ion **2a** by methanol is demonstrated. Finally, LIS values are in agreement with an anti relationship between the methoxy group and the cyclobutene ring.

To complete the rationalization of our results it must be assumed, and we propose, that formation and/or trapping of **2b** (Scheme 2) is much slower than that of **2a**. The positive charge in **2a** can experience rearside nucleophilic solvation by methanol from the very beginning of its coming into being whereas inspection of the outside region of the cationic centre in **2b** shows how that side is shielded by the cyclobutene ring.

But, what about a direct nucleophilic solvent participation in the heterolysis of carbon-carbon bond of **4**, that is a SN_2 one step formation of **13** from **4**? If this were the case the methanolysis would exhibit a rate increase under basic conditions. Indeed compound **4** reacted readily ($\simeq$ 30 minutes) with methanol in the presence of potassium carbonate at r.t. but the reaction outcome was completely different from that observed under neutral conditions. Neither **14** nor **15** were detected in the reaction mixture and an 1:2 adduct of **4** and methanol, i.e. **16** (Scheme 2), was isolated in good yields. The strong IR absorption for C = N bond [ν_{max} 3365 and 3120 (s, NH_2), 2230 (w, CN), 1680 (s, C = N)] and the easy hydrolysis under acidic conditions to the imide **17a** [ν_{max} 3240 (s, NH), 2240 (w, CN), 1790 and 1735 (s, CO) cm^{-1}] suggests the involvement of two cis cyano groups to give a product containing an amidine (or imidic ester) function. Accordingly the preferred site of a direct nucleophilic attack (at least by a charged nucleophile) on **4** is a cyano group and not the carbon atom at position 10, which becomes the most reactive one only upon formation of **2a**.

Aiming further at substantiating the peculiar behaviour of **4**, we investigated the reaction of methanol with **6a** (≡ **6**) and other tetracyanosubstituted hydrocarbons such as **18a** and **19a**. (Scheme 3)

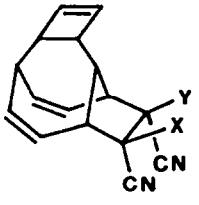
The addition of methanol to **18a** in the presence of potassium carbonate was very fast and exothermic giving only **18b**. The ^{13}CNMR spectrum [**18b** δ(DMSO) 12.7, 14.3 and 15.15 (three d, C-2 C-3 and C-4), 29.95 (t, C-5) 38.15 (d, C-6), 48.75 and 49.55 (two d, C-1 and C-7), 50.1 and 51.2 (two q, OMe), 60.6 and 61.25 (two s, C-8 and C-9), 116.7 (s, MeO-C-OMe), 118.1 and 119.45 (two s, CN), 160.75 (s, H_2N-C=N)] as well as the ^{1}HNMR spectrum support the cyclic structure **18b** and rule out the open chain symmetric structure **18c**. The chemical shift of NH_2 protons [δ(DMSO) 7.32 (2H, bs which

was exchanged by D_2O] and the small differences of chemical shifts of the two methoxy groups in the NMR [^{1}HNMR : δ (DMSO) 3.27 and 3.35] spectra are consistent with the ketal-amidine structure **18b** whereas they are in contrast with the alternative hemiaminal-imidic ester structure **18d**. Bis-adduct **18b** was selectively hydrolyzed to the iminopyrrolidinone **18e** with MeOH/silicagel whilst under more drastic conditions the imide **18h** was obtained. Compounds **18h** was quantitatively methylated with excess diazomethane to **18i** whilst **18e** gave a mixture of **18f** (major) and **18g**. The symmetry plane in **18h, i** is clearly disclosed by their ^{1}HNMR and ^{13}CNMR spectra [e.g. ^{13}CNMR of **18i**: δ (DMSO) 14.36 (d, C-2 and C-3), 15.81 (d,C-4), 26.65, q, Me), 31.2 (t, C-5), 37.65 (d, C-6), 51.65 (d, C-1 and C-7), 55.0 (s, C-8 and C-9), 115.4 (s, CN), 169.4 (s, CO)] .

Formation of **18b** (and other 1:2 adducts) involves addition of one molecule of methanol to a CN group followed by ring closure to **18j**[25,26] and addition of a second molecule of methanol to this cyclic monoadduct.[27]

The reactions of MeOH with **6a** and **19a** too under basic conditions were exothermic to give bis-adducts **6b** and **19b**, respectively, whose spectroscopic data and chemical reactivity are similar to that described above for **18b**.

Methanol additions under neutral conditions were much slower (2-7 days at 40°C. Reactivity order: **18a** > **19a** ≥ **6a**) and revealed how sensitive these reactions are to base catalysis: in fact longer reaction times were observed when reaction flasks were washed with concentrated hydrochloric acid to remove eventual traces of base. Once again only products resulting from an attack at the cyano groups were detected. The addition of methanol to **6a** and **18a** did not take place under acidic conditions (pH ≃ 3). Therefore "glass" catalysis seems to be at work under neutral conditions.



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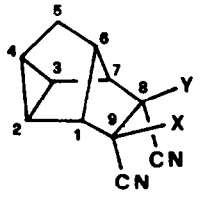

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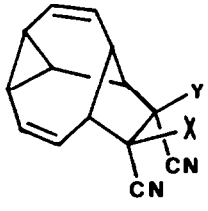

19

a : X , Y = CN

b : X–Y = $\begin{matrix} & OMe & \\ & | & \\ C & -N= & C \\ | & & | \\ OMe & & NH_2 \end{matrix}$

c : X , Y = $\begin{matrix} C=NH \\ | \\ OMe \end{matrix}$

d : X–Y = $\begin{matrix} & OMe & \\ & | & \\ C & -N= & C \\ | & & | \\ NH_2 & & OMe \end{matrix}$

e : X–Y = $\begin{matrix} C & -N- & C \\ \| & | & \| \\ O & H & NH \end{matrix}$

f : X–Y = $\begin{matrix} C & -N- & C \\ \| & | & \| \\ O & Me & NH \end{matrix}$

g : X–Y = $\begin{matrix} C & -N- & C \\ \| & | & \| \\ O & Me & NMe \end{matrix}$

h : X–Y = $\begin{matrix} C & -N- & C \\ \| & | & \| \\ O & H & O \end{matrix}$

i : X–Y = $\begin{matrix} C & -N- & C \\ \| & | & \| \\ O & Me & O \end{matrix}$

j : X–Y = $\begin{matrix} C=N- & C \\ | & \| \\ OMe & NH \end{matrix}$

Scheme 3

The series of compounds **6h, i, 18e-i,** and **19h,i** were found homogeneous by ^{1}HNMR and TLC techniques. In our opinion of the two diastereotopic pairs of cyano groups in **6a, 18a** and **19a** that one on the less crowded side of the molecule was preferentially attacked by MeOH.[28] Moreover the different crowding felt by reacting cyano groups can be advanced as a reasonable explanation of the higher reaction rate of **18a** than that of **19a** and **6a** which in turn is higher than that of **4.**

As far as compound **4** is concerned we conclude that the lucky coincidence of i) a low reactivity of cyano groups due to steric hindrance under neutral conditions ii) an easy formation of dipolar ion **2a** iii) a nucleophilic attack on **2a** faster than its further rearrangements made our trapping experiments successful.

The heterolysis of carbon-carbon bond in **4** conforms to a SN_1 reaction scheme without direct nucleophilic solvent attack[29] but resulting in a zwitterion stabilized by nucleophilic and electrophilic solvation.[30] Moreover one can argue that the easy formation of **2** from **4** takes advantage of the fact that cyclopropyl residues can fully exploit their stabilization effect on the developing positive charge with concomitant slight reduction of angle strain. By contrast in the transition state leading to **2** from **1** and TCNE the stabilization of the positive charge is much less than that in **2** and is partly counteracted by increase in angle strain.

CONCLUSION

As well known homo-Diels-Alder reaction is generally considered to go via a symmetry allowed concerted process.[31] Absence of polarity solvent effects on reaction rate,[21,32] retention of configuration in the reactions of norbornadiene with cis and trans disubstituted dienophiles,[33] high negative activation volume in the reaction of norbornadiene with TCNE[32] support this view and militate against a stepwise (diradical or ionic) process. Polarity solvent effects on product ratios arising from competition between homo-Diels-Alder and genuine ionic two step cycloadditions has been also interpreted in terms of concertedness[1b,21] of the former reaction.

However the great influence of solvent polarity on the rate constant which co-occurred with no solvent effect on product ratios led the Authors to propose an ionic mechanism for the homocycloaddition of TCNE to hexamethyl (Dewar benzene).[34] This same mechanism was also advanced as a reasonable alternative to the concerted one on speculative basis by other Authors.[2,4] The results of the present study represent evidence that formation of a stabilized cationic centre can promote a heterolytic reaction in a homocycloadduct to give a zwitterion which is a reasonable intermediate in the cycloaddition-cycloreversion process.

The solvent effect on product ratios, the low enhancement of the homocycloaddition rate induced by increased solvent polarity and the outcome of acid catalyzed methanol addition to **1** support a concerted asynchronous formation of **4.** Concerted cleavage of this adduct is in competition with a side blind alley formation of the zwitterion **2.** This latter pathway is the favoured one in protic polar solvents able to trap **2** [i.e. **1**+TCNE $\rightleftarrows$ **4** $\rightleftarrows$ **2** $\rightarrow$ **13**].

However we cannot claim to have found conclusive evidence against a two step reaction [i.e. **1** + TCNE $\rightleftarrows$ **2** $\rightleftarrows$ **4**]. We are clearly dealing with a borderline case of homo-Diels-Alder reaction.

EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were made on a Carlo Erba CHN analyzer mod. 1106. IR spectra were measured as Nujol suspensions on a Perkin Elmer 157 spectrophotometer and UV spectra on a Perkin-Elmer 200 spectrophotometer. ^{1}H and ^{13}CNMR spectra were recorded on a Bruker WP80SY spectrometer (operating at 80 and 20.2 MHz) equipped with an Aspect 2000 computer with

tetramethylsilane as internal standard. Mass spectra were measured on a Du-Pont 21-492B using electron impact and chemical ionization modes. Thin layer chromatography was carried out on plates precoated with Silicagel 60 GF_{254} Merck. Spots of all of the compounds could be detected by spraying with 3% chromic oxide in sulphuric acid (50%) followed by heating at 120°C. Compounds **1**, **14** and **15** could also be revealed under UV light (254 nm). Column chromatography were performed with Silicagel 60 (70-230 mesh) Merck eluting with cyclohexane-ethyl acetate mixtures. Benzene, nitromethane and methanol were dried and distilled before use. Tetracyanoethene was purified by crystallization from 1,2-dichloroethane.

Reaction of **1** with tetracyanoethene. Compound **1** (0.195 g, 1.25 mmol) in benzene (1 ml) was added to a yellow solution of tetracyanoethene (0.128 g, 1.0 mmol) in benzene (5 ml). The resulting brown-yellow reaction mixture was kept ad 21°C for twenty days. The colour slowly faded with time and a crystalline product progressively precipitated from the reaction mixture. The precipitate (0.205 g, 72%) was filtered off and analyzed by ^{1}HNMR and IR techniques. Only signals due to compound **4** were detected in the ^{1}HNMR spectrum and the strong and characteristic absorptions of compound **6** were completely absent in the IR spectrum of this product. The mother liquors were concentrated under reduced pressure and the residue purified by column chromatography to give a product (0.060 g, 21%) which was shown to be a mixture (5.0:1) of **4** and **6** on the basis of IR and ^{1}HNMR analysis. The R_F values of compounds **4** and **6** are very similar and we did not manage to separate them satisfactorily by column chromatography. Compound **4** decomposed on attempted GLC (capillary column, at 100°C). Compound **4** was purified as colurless prisms from ethyl acetate, m.p. 185-6°C. (Found: C, 75.4; H, 4.4; N, 19.6. Calc. for $C_{18}H_{12}N_4$: C, 76.0; H, 4.3; N, 19.7). IR: ν max 2240 (w), 855 (s), 825 (s) and 770 (s) cm^{-1}. Mass spectrum (75 eV, the compound was vaporized at 60°C); m/z 284 ($M^{+\cdot}$, 1%), 283 (2%), 156 ($C_{12}H_{12}^{+\cdot}$, 10%), 155 ($C_{12}H_{11}^{+}$, 21%), 128 ($C_6N_4^{+\cdot}$, 40%), 91 (100%).

The reaction above was repeated under otherwise same conditions with an excess of TCNE (1.25 molar equivs.). After 20 days TLC analysis showed that compound **1** had completely disappeared. Yields and product ratios duplicated that found in the first reaction. A third experiment (with excess TCNE) was carried at 45°C. The reaction went to completion within 150 hrs (89%, ratio **4**:**6** = 24).

A parallel set of three experiments was carried out in nitromethane. The reactions at 21°C went to completion within 24 hrs and that at 45°C within 6 hrs. In all of the cases the solvent was evaporated off and the residue purified by column chromatography to afford a mixture of **4** and **6** (**4**:**6** = 7:3, 69%).

The formation of small amounts of brown-yellow by-products, in particular in nitromethane, prevented accurate rate measurements by usual photometric techniques.

In order to prepare pure **6**, a solution of **1** (0.182 g, 1.17 mmol) and TCNE (0.182 g, 1.42 mmol) in nitromethane (3 ml) was heated at 90°C in a sealed ampoule for 35 hrs. Usual work-up of the resulting dark-brown solution furnished **6** (0.132 g, 40%). Compound **6** crystallized as colourless prisms from ethyl acetate, m.p. 202-3°C. (Found: C, 75.5, H, 4.5; N, 19.6). IR: ν max 2240 (vw), 850 (s), 800 (s) and 755 (s) cm^{-1}. Mass spectrum (75 eV, the compound was vaporized at 50°C): m/z 284 ($M^{+\cdot}$, 18%), 283 ($M-1^{+}$, 77%), 257 (50%), 156 ($C_{12}H_{12}^{+\cdot}$, 100%), 155 ($C_{12}H_{11}^{+}$, 79%), 128 ($C_6N_4^{+\cdot}$, 20%), 91 (78%).

Finally solid TCNE (0.112 g) was added to a stirred mixture of **1** (0.110 g) and hexafluoropropanol (2 ml) under mild cooling with water. There was a slight evolution of heat whilst the reaction mixture turned from yellow to dark-brown. After 3 hrs at r.t. no **1** could be detected by TLC analysis. A mixture (45:55) of **4** and **6** (0.077g, 38%) was the only isolated product.

Cycloreversions of compounds **4** and **6**. Compound **4** (0.140 g) in benzene (5 ml) was heated in a sealed ampoule at 90°C for 150 hrs. Column chromatography permitted us to isolate compound **1** (0.010 g) and mixture (1.3:1.0) of **4** and **6** (0.070 g).

A solution of **4** (0.150 g) and TCNE (0.020 g) in nitromethane (4 ml) was heated at 90°C for 45 hrs. After usual work up of the resulting dark-brown reaction mixture, compound **6** (0.057g, 38%) was isolated in a pure state.

A solution of **6** (50 mg) in nitromethane and benzene was heated at 90° for 45 and 150 hrs, respectively. Compound **6** was then recovered in 85% and 90% yields and no **1** could be detected in the reaction mixtures by TLC analysis or by its characteristic smell.

Reaction of **1** with TCNE in methanol. A deep brown-yellow colour developed at once when TCNE (80 mg) was added to a solution of **1** (80 mg) in methanol (5 ml) and then faded to a light brown-yellow one within twenty five minutes. After 3 days TLC analysis showed that **1** had completely disappeared whilst two products, which did not absorb at 254 nm but were efficiently detected upon spraying plates with CrO_3/H_2SO_4, were present in the reaction solution.

Usual work up and column chromatography afforded 60 mg of the first spot which was shown by ^{1}HNMR to be a mixture (2:3) of **11a** and **11c** and 6 mg of the second one **11b**.[22]

Products arising from the reaction of TCNE with methanol were not characterized.

To a yellow solution of methyl orange in methanol TCNE (purified once by crystallization and twice by sublimation) was added. The solution turned red at once indicating that the medium had become acidic.

Reaction of **4** with methanol under neutral conditions. A solution of **4** (0.155 g) in anhydrous methanol (25 ml) was kept at 40°C for 3 days. The solvent was evaporated off under reduced pressure to give a residue which was repeatedly dissolved in cyclohexane-benzene and filtered to remove small amounts of tarry products and unreacted **4**. Careful evaporation of the filtrate furnished a mixture (≃ 1:1) of only two products, i.e. **13** and **14**. The presence of **13** was clearly apparent from the ^{1}HNMR (C_6D_6) spectrum in which a singlet at δ 5.77 and a triplet at δ 4.30 (J = 6.5 Hz) attributable to H-4, H-5 and to H-12, respectively, of **13** are visible. Moreover, in addition to the signals of **14**, six signals [δ ($CDCl_3$) 15.6, 18.0 and 18.2 (three d, C-1, C-2, C-7, C-8, C-9 and C-11), 35.6 (d, C-10), 43.6 (d, C-3 and C-6), 72.6 (d, C-12)] were present in the aliphatic region of the ^{13}CNMR spectrum. Their chemical shifts are very similar to the chemical shifts of the ten carbon atoms of the saturated carbocyclic moiety of **14** (see General Part). Two more signals in the same region [δ 29.3 (d) and 46.7 (s)] and two low intensity singlets at δ 107.6 and 110.9 were attributed to the disubstituted and trisubstituted carbon atoms and to cyano groups, respectively, of the tetracyanoethyl moiety of **13**. C-4, C-5 and OMe accidentally resonated at the same chemical shift in both compounds. Column chromatography of the above mixture afforded pure **14** (0.066 g, 42%) as the only isolated product Colourless platelets from cyclohexane, m.p. 133-135°C (Found: C, 74.85; H, 5.1; N, 14.4. Calc. for $C_{18}H_{15}N_3O$: C, 74.7; H, 5.2; N, 14.5). Mass spectrum: 289 ($M^{+\cdot}$).

Further experiments showed that the ratio of **13** and **14** was highly dependent on the reaction and work up conditions. For example, a slurry of **4** (0.015 g) and tetradeuteromethanol (0.6 ml) was left at 30°C for five days, then cooled to -30°C and filtered to remove insoluble unreacted **4**. ^{1}HNMR analysis of the solution showed the presence of **13** [δ 1.45 (6H, m), 3.42 (s, H-10), 3.60 (bs, H-3 and H-6), 4.60 (t, H-12, J = 6.3 Hz) 6.23 (s, H-4 and H-5)] along with small amounts (≤ 10%) of **14** (singlet at δ 3.94 due to H-10).

The reaction of **4** with methanol to give **13** and **14** took also place (TLC analysis) under acidic conditions (pH ≃ 3).

LIS values of **14** were measured for $CDCl_3$ solutions using Eu(fod)3 as reagent shift: Δ_M (ppm) 0.13 (H-4 and H-5), 0.19 (H-9 and H-11), 0.27 (H-10), 0.35 (H-2 and H-7), 0.37 (H-3 and H-6), 0.38 (Me), 0.45 (H-1 and H-8), 0.60 (H-12). Although the ability of **14** to coordinate the reagent shift is quite low, the measured values indicate that the preferred coordination site is the methoxy group. In fact the largest shift is experienced by H-12.

Synthesis of **15**. The UV spectrum of a solution of **4** (1.73 mg) in methanol (50 ml) showed end absorption only. After 12 days at r.t. this solution exhibited a maximum at 255 nm with an ε ($\log\varepsilon$ = 4.11) value only slightly lower than that expected on the basis of a quantitative conversion **4**→**15**. A similar result was obtained for a solution of **14** (1.25 mg in 50 ml of methanol) after 30 hrs. Either one solution was evaporated to give **15** (TLC, IR).

On a preparative scale a solution of **14** (0.040 g) in methanol (150 ml) was kept at r.t. for 60 hrs. After that time TLC analysis showed that conversion **14** → **15** was ≤ 30%. Addition of 2 ml of methanol saturated with potassium carbonate led to the complete disappearance of **14** within two hours. Compound **15** was purified by column chromatography (0.022 g, 54%) [Colourless leaflets from cyclohexane, m.p. 139-141°C. (Found: C, 73.4; H, 6.2; N, 9.4. Calc. for $C_{18}H_{18}N_2O_2$: C, 73.4; H, 6.2; N, 9.5). Mass spectrum: 294 ($M^{+\cdot}$). ^{1}HNMR: δ ($CDCl_3$) 1.21 (m, cyclopropyl protons), 3.43 (s, MeO), 3.58 (m, H-3 and H-6), 4.03 (s, H-10), 4.35 (s, MeO), 4.46 (t, H-12, J = 6.3 Hz), 6.15 (s, 2H, H-4 and H-5)].

Reaction of **4** with methanol under basic conditions. To a slurry of **4** (0.075 g) and methanol (1 ml) methanol (0.5 ml) saturated with potassium carbonate was added. The solid **4** slowly dissolved to give a clear solution within ≃ 30 minutes. Then a new compound, **16**, started precipitating and was separated by suction filtration after 2 hrs (0.035 g). The mother liquors were evaporated and the residue rapidly washed with cold methanol/water to give a further crop of **16** (25 mg, total yield 65%). **16**: m.p. ≃ 145°C dec. (Found: C, 70.20; H, 6.0; N, 16.4. Calc. for $C_{20}H_{20}N_4O_2$: C, 68.95; H, 5.8; N, 16.1). ^{1}HNMR: δ (DMSO) 0.50 - 1.53 (m, 6H, cyclopropyl protons), 3.28 and 3.43 (two s, OMe) 3.00 - 3.70 (m, 4H, H-3, H-6, H-10 and H-12), 6.27 (bs, 2H, H-4 and H-5), 7.38 (bs, 2H which were exchanged by D_2O).

Synthesis of **17a** and **17b**. Diluted hydrochloric acid (10%, 1.0 ml) was added to a solution of **16** (40 mg) in methanol (2 ml) and the resulting reaction mixture left aside at r.t. for 12 hrs. Then the solution was diluted with water, the precipitated **17a** separated by suction filtration [21 mg, 60%; m.p. 230°C dec. (Found: C, 70.8; H, 4.35; N, 13.8 Calc. for $C_{18}H_{13}N_3O_2$: C, 71.3; H, 4.3; N, 13.9). IR: ν max 3240 (s), 2240 (w), 1795 (m), 1735 (vs)] and transformed into **17b** [colourless needles from benzene-petrol ether, m.p. 208-209°C. (Found: C, 69.5; H, 4.8; N, 12.4. Calc. for $C_{19}H_{15}N_3O_2 \cdot \frac{1}{2} H_2O$: C, 69.9; H, 4.9; N, 12.9). Mass spectrum: 318 [M+1]$^+$. ^{1}HNMR: δ ($CDCl_3$) 0.80 (m, 2H), 1.15 (m, 1H) 1.58 (m, 3H), 3.15 (s, 3H), 3.65 (m, 4H), 6.23 and 6.30 (two d, 2H, H-4 and H-5, J 4,5 = 3.0 Hz). IR: ν max 2240 (w), 1790 (m) and 1710 (vs) cm^{-1}] by treatment with diazomethane.

Reactions of **18a** with methanol. Methanol (0.1 ml) saturated with potassium carbonate was added to an ice cooled slurry of **18a**[35] [^{1}HNMR: δ (DMSO) 1.58 (m, 3H, H-2, H-3, H-4), 1.80 (bs, 2H, H-5), 2.52 (bs, 1H, H-6), 3.37 (m, 2H, H-1 and H-7); ^{13}CNMR: δ (DMSO) 12.8 (d, C-2 and C-3) 15.20 (d, C-4), 31.5 (t, C-5), 41.5 (d, C-6), 46.9 (s, C-8 and C-9), 54.7 (d, C-1 and C-7), 112.4 and 113.0 (s, CN)] (0.250 g) and methanol (3 ml). Compound **18a** dissolved rapidly in an exothermic reaction

and compound **18b** started precipitating as beautiful colourless prisms after ~ 2-3 minutes. The reaction mixture was cooled to -30°C and compound **18b** separated by suction filtration [260 mg, 80%; m.p. ≃ 150°C dec. (Found: C, 63.2; H, 5.7; N, 19.5. Calc. for $C_{15}H_{16}N_4O_2$: C, 63.4; H, 5.7; N, 19.7). IR: ν max 3380 and 3060 (broad strong bands, NH_2), 2240 (w, CN), 1678 (s, C = N), 1640 (m) cm^{-1}. ^{1}HNMR: δ (DMSO) 1.41 (m, 3H, H-2, H-3 and H-4), 1.60 (bs, 2H, H-5), 1.75 (bs, 1H, H-6), 2.59 and 2.80 (two bs, H-1 and H-7), 3.27 and 3.35 (tw s, OMe), 7.32 (bs, 2H, NH_2)].

TLC analysis of a reaction carried out under neutral conditions (0.250 g of **18a** in 5 ml of methanol at 40°C) showed the disappearance of **18a** after ≃ 48 hrs and the formation of **18b** along with small amounts of **18e**. The presence of **18e** as a by-product was also apparent from the IR spectrum of the crude residue after evaporation of the solvent.

A third reaction was conducted in a flask previously washed with concentrated hydrochloric acid and then with methanol. Compound **18a** disappeared after ≃ 6 days and once again TLC analysis showed the formation of **18b** along with minor amounts of **18e**.

Finally, to a yellow solution of **18a** (0.250 g) in methanol (5 ml), containing a trace of methyl orange, a solution of anhydrous hydrochloric acid in methanol was added until the colour turned red. Compound **18a** was quantitatively recovered upon evaporation of the solvent after fifteen days at 40°C.

Synthesis of **18e-i**. A solution of **18b** (0.550 g) in methanol was adsorbed on Silicagel H (70-230 mesh) Merck (40 g) and kept at 40°C for 24 hrs in the air. The resulting dry Silicagel was then poured in a column with a fritted glass bed support and eluted with ethyl acetate. Evaporation of ethyl acetate furnished pure **18e** (0.455g, 99%), which started decomposing without melting at ≃ 300°C. (Found: C, 65.8; H, 4.1; N, 23.2; Calc. for $C_{13}H_{10}N_4O$: C, 65.5; H, 4.2; N, 23.5). IR: ν max 3240 (broad band, NH), 2240 (w), 1730 (s), 1680 (s) and 1540 (s) cm^{-1}. ^{1}HNMR: δ (DMSO) 1.59 (bs, H-2, H-3 and H-4), 1.67 (bs, H-5), 2.86 and 2.87 (two bs, H-1 and H-7), 9.69 (broad signal exchanged by D_2O, 2H, NH), the signal of H-6 is overlapped by the signal of H-5 at δ 1.65.

An excess of diazomethane (ether solution) was added to a solution of **18e** (0.200 g) in methanol (15 ml). There was a brisk evolution of nitrogen, then the solvent was evaporated off and the residue column chromatographed to give **18f** [0.180 g, 85%; colourless prisms from ethyl acetate, m.p. 213-5°C (Found: C, 66.4; H, 4.9; N 22.4. Calc. for $C_{14}H_{12}N_4O$: C, 66.65; H, 4.8; N, 22.2). IR: ν max 3280 (m, NH), 2240 (w), 1740 (s, CO), 1655 (vs, C = N). ^{1}HNMR: δ($CDCl_3$), 1.75 (m, 5H, H-2 - H-6), 2.74 and 2.88 (two bs, H-1 and H-7), 3.18 (3H, Me), 8.41 (broad signal exchanged by D_2O, 1H, NH)] and **18g** [0.018 g, 8%; colourless prisms from MeOH, m.p. 170-171°C (Found: C, 67.6; H, 5.3; N, 21.1. Calc. for $C_{15}H_{14}N_4O$: C, 67.65; H, 5.3; N, 21.0)].

Compound **18f** did not afford **18g** upon treatment with diazomethane.

Compound **18b** and **18e**, respectively, could be easily hydrolyzed under acidic conditions (100 mg, of **18b** or **18e** 6 ml of MeOH and 2 ml of 10% HCl at r.t. for 12 hrs) to **18h** [≥80% yields, colourless platelets from MeOH/H_2O m.p. 308-310°C. (Found C, 64.9; H, 3.8; N, 17.6. Calc. for $C_{13}H_9N_3O_2$: C, 65.3; H, 3.8; N, 17.6). IR: ν max, 3300 (s, NH), 2240 (w, CN), 1795 (m) and 1738 (vs, CO) cm^{-1}. ^{1}HNMR: δ (DMSO) 1.60 (bs, 3H, H-2, H-3 and H-4), 1.69 (bs, 2H, H-5), 2.05(bs, 1H, H-6), 2.79 (bs, 2H, H-1 and H-7), 12.75 (very broad band, exchanged by D_2O,1H, NH). ^{13}CNMR: δ (DMSO) 13.8 (d, C-2 and C-3), 15.25 (d, C-4), 30.8 (t, C-5), 37.4 (d, C-6), 51.0 (d, C-1 and C-7) 55.5 (s, C-8 and C-9), 115.1 (s, CN), 169.05 (s,CO)].

Acidic hydrolysis of **18f** and **18g** produced **18i** [≥85% yields; colourless needles from ethyl acetate, m.p. 254-255°. (Found; C, 66.4, H, 4.5; N 16.7. Calc. for $C_{14}H_{11}N_3O_2$: C, 66.4; H, 4.4; N, 16.6). IR: νmax 2240 (w, CN),1795 (w) and 1710 (vs, CO) cm^{-1}. ^{1}HNMR: δ (DMSO) 1.62 (m, 5 H, H-2, H-3, H-4 and H-5) , 2.12 (bs, 1H, H-6), 2.81 (bs, 2H, H-1 and H-7), 2.94 (s, Me)] .

Synthesis of **6b -i and 19b - i**. Methanol saturated with potassium carbonate (0.5 ml) was added to a slurry of **6** (32 mg) and methanol (1 ml) at r.t. The solid dissolved rapidly in a slightly exothermic reaction. After five minutes the solvent was evaporated off and the residue washed with cold methanol/water to give **6b** (36 mg, m.p. ≃ 140°C dec.). Due to its high propensity to include solvents we could not obtain good analytical data for **6b** [I.R.: ν max 3340 and 3150 (broad bands, NH_2), 2240 (w), 1675 (s, C=N) and 1605 (m)] . Compound **6b** was quantitatively converted into **6e** with Silicagel [**6e** started decomposing at ≃ 310°C. (Found: C, 71.2; H, 4.3; N, 18.9. Calc. for $C_{18}H_{14}N_4O$: C, 71.5; H, 4.7; N, 18.5). IR: ν max 3300 (broad, NH); 2240 (w), 1730 (m), 1660 (s) and 1548 (s) cm^{-1}. ^{1}HNMR: δ (DMSO) 2.90-3.50 (m, 6H), 5.50-6.50 (m, 6H), 9.75 (broad signal exchanged by D_2O, 2H, NH)] .

The reaction under neutral conditions took place in ≃ 7-10 days at 40°C. Evaporation of methanol allowed us to isolate the hydrolysis product **6e** in quantitative yield. The same product was obtained after ≃15 days at 40°C when the reaction was carried out in a flask previously washed with concentrated hydrochloric acid.

Methanol did not add to **6** under acidic conditions (pH ≃ 3, 15 days at 40°C).

Treatment of **6e** with diazomethane gave rise to a mixture (≃ 1:1) of two regioisomeric monomethyl derivatives **6f** separated by column chromatography (80%; higher R_F compound m.p. 235-240°C, lower R_F compound m.p. 225-230°C) along with minor amounts of by-products (probably dimethyl derivatives). Compounds **6f** showed very similar IR [**6f** (lower R_F): ν max 3290 (m), 2240 (w), 1750 (s) and 1665 (vs) cm^{-1}] and ^{1}HNMR [**6f** (lower R_F):δ($CDCl_3$) 2.60 (m, 1H, H-6), 3.10- 3.50

(m, 5H), 3.25 (s, Me), 5.80 (m, 1H), 5.98 (m, 1H) 6.05 and 6.15 (two d, H-3 and H-4, J 3,4 = 3.0 H2), 6.46 (m, 1H)] spectra and, both, could be hydrolyzed to **6i** [colourless needles from ethyl acetate m.p. 220-225°C. Mass spectrum: 318 $[M+1]^+$. IR: ν max 2240 (w, CN), 1790 (m) and 1710 (vs) cm^{-1}. ^{1}HNMR: δ (DMSO) 2.80 (m, 1H, H-6), 3.00 (s, Me), 3.10-3.50 (m, 5H), 5.68 (dd, 2H, H-11 and H-14, J10,11 = J7,14 = 5.0 Hz and J11,12 = J13,14 = 12.0 Hz), 6.01 and 6.17 (two d, H-3 and H-4, $H_{3,4}$ = 3.0 Hz), 6.10 and 6.42 (two m, H-12 and H-13, J1,12 = J1,13 = 10 Hz)]

Compound **6i** was also prepared (70-80%) from **6b** and **6e** via **6h** [**6h**: m.p. ≃ 250°C dec.; IR: ν max 3250 (s), 2240 (w), 1795 (m) and 1700 (s) cm^{-1})].

The reaction of **19a** with methanol produced **19b** under basic conditions (exothermic reaction) and **19b** along with minor amounts of **19e** under neutral conditions (5 days at 40°C) [**19b**: m.p. ≃ 135°C dec. IR: νmax 3340 (s) and 3100 (m), 2240 (w), 1680 (vs) and 1620 (m) cm^{-1}].

Compound **19b** (or the mixture **19b** + **19e**) treated with hydrochloric acid in methanol/water gave **19h** [76%; colourless needles from methanol-water, m.p. 306-308°C (Found: C, 69.5; H, 4.0; N, 15.7. Calc. for $C_{14}H_{11}N_3O_2$: C, 69.3; H, 4,0; N, 15.2) I.R: ν max 3260 (broad strong band), 2240 (w), 1800 (m), 1730 (vs) cm^{-1}] which was quantitatively methylated to **19i** [colourless needles from benzene petrolether, m.p. 219-220°C. IR: ν max 2240 (W), 1798 (m) and 1720 (vs) cm^{-1}. ^{1}HNMR: δ ($CDCl_3$) 2.00-2.70 (m, 3H), 3.06 (m, 1H), 3.20 (s, Me), 3.43 (m, 1H), 5.65 - 6.25 (m, 4H)] with diazomethane.

Crystal data and X-ray structure refinement. **6**: $C_{18}H_{12}N_4$, colourless crystals, monoclinic, space group P21/n; a = 12.048 (1) c = 7.111 (1) A; ß = 93.97 (1)°; V = 1437.7 A^3; Z = 4; D_c = 1.314 $g:cm^3$; F(000) = 592; μ = 0.760 cm^{-1}. Intensity data were collected on a Philips PW 1100 four-circle diffractometer using the ω scan technique and Mo $K\alpha$ radiation (λ = 0.7107 A). Two equivalent monoclinic reflections were collected in the ϑ range 2-20°. They were corrected for Lorentz and polarisation factors and for absorption following the semi-empirical method of North et al.[36] Then the equivalent pairs were merged. The structure was solved by direct methods,[37] and isotropically refined by a fully-matrix least-squares procedure by using a locally modified version of the program ORFLS.[38] 759 reflections with $I \geq 3\sigma(I)$, out of the 1341 independente reflections, were regarded as observed during the refinement. Coordinates for hydrogen atoms were calculated on the basis of geometrical considerations and inserted with an overall thermal factor of 5 A^2. The anisotropic refinement was performed by varying positional and thermal parameters of only the non-hydrogen atoms. A new set of coordinates for the H atoms was then calculated and inserted in the least-squares procedure. The final unweighted R index for the observed reflections was 4.0 %.[39] Scattering factors were those listed in the International Tables for X-ray Crystallography. Atomic coordinates, equivalent isotropic parameters, bond distances and angles for the non-hydrogen atoms are listed in Tables 1-3. The results of the anisotropic refinement are shown in the Figure which depicts the 20% probability ellipsoids.[40]

Tables of anisotropic thermal parameters and torsion angles for non-hydrogen atoms together with final atomic coordinates for hydrogens and a list of observed and calcucated structure factors have been deposited at the Cambridge Crystallographic Data Centre.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors (A^2) for non hydrogen atoms. E.S.d. in parentheses

ATOM	X/A	Y/B	Z/C	B-EQUIV.
C1	0.8275 (4)	0.2888 (2)	0.8513 (6)	2.65 (13)
C2	0.7987 (4)	0.2424 (2)	1.0395 (6)	2.28 (12)
C3	0.7532 (4)	0.3107 (2)	1.1605 (6)	2.60 (12)
C4	0.6771 (3)	0.3532 (3)	1.0137 (5)	2.59 (13)
C5	0.7452 (4)	0.3628 (2)	0.8377 (5)	2.66 (13)
C6	0.8056 (4)	0.4392 (3)	0.8106 (6)	3.29 (15)
C7	0.8338 (4)	0.4955 (3)	0.9320 (6)	3.72 (15)
C8	0.8103 (4)	0.4976 (3)	1.1405 (6)	3.37 (15)
C9	0.8724 (4)	0.4322 (3)	1.2504 (6)	3.19 (16)
C10	0.8481 (4)	0.3561 (3)	1.2582 (5)	2.78 (16)
C11	0.6158 (4)	0.4271 (3)	1.0742 (6)	3.01 (13)
C12	0.5711 (4)	0.4225 (3)	1.2676 (7)	4.40 (18)
C13	0.6330 (5)	0.4813 (3)	1.3385 (6)	4.09 (17)
C14	0.6839 (4)	0.4991 (3)	1.1546 (6)	3.56 (15)
C15	0.8128 (4)	0.2361 (3)	0.6838 (7)	3.37 (15)
C16	0.9463 (5)	0.3118 (3)	0.8649 (6)	3.36 (15)
C17	0.8974 (4)	0.2005 (3)	1.1247 (6)	2.98 (15)
C18	0.7105 (4)	0.1829 (3)	0.9934 (6)	2.95 (15)
N19	1.0379 (4)	0.3247 (3)	0.8700 (6)	5.61 (16)
N20	0.8013 (4)	0.1959 (2)	0.5551 (6)	5.05 (15)
N21	0.9737 (4)	0.1686 (2)	1.1862 (6)	4.25 (12)
N22	0.6437 (4)	0.1366 (3)	0.9569 (6)	4.82 (15)

Table 2. Bond lenghts for non-hydrogen atoms (Å; estimated standard deviation in parentheses).

C1	- C2	1.608 (6)	C4	- C5	1.551 (6)	C11	- C14	1.550 (6)
C1	- C5	1.590 (6)	C4	- C11	1.523 (6)	C12	- C13	1.318 (7)
C1	- C15	1.486 (6)	C5	- C6	1.496 (6)	C13	- C14	1.512 (7)
C1	- C16	1.479 (7)	C6	- C7	1.311 (7)	C15	- N20	1.138 (6)
C2	- C3	1.557 (6)	C7	- C8	1.529 (6)	C16	- N19	1.123 (7)
C2	- C17	1.475 (6)	C8	- C9	1.516 (6)	C17	- N21	1.128 (6)
C2	- C18	1.479 (7)	C8	- C14	1.534 (7)	C18	- N22	1.137 (7)
C3	- C4	1.520 (6)	C9	- C10	1.315 (7)			
C3	- C10	1.505 (6)	C11	- C12	1.513 (7)			

Table 3. Bond angles for non-hydrogen atoms (°; estimated standard deviation in parentheses).

C15	- C1 - C16	105.7 (4)	C4	- C3 - C10	118.7 (4)	C4	- C11 - C14	119.2 (4)
C5	- C1 - C16	113.3 (4)	C3	- C4 - C11	118.1 (3)	C4	- C11 - C12	115.1 (4)
C5	- C1 - C15	112.3 (3)	C3	- C4 - C5	106.0 (3)	C12	- C11 - C14	85.3 (3)
C2	- C1 - C16	109.7 (3)	C5	- C4 - C11	115.9 (3)	C11	- C12 - C13	94.7 (4)
C2	- C1 - C15	110.9 (3)	C1	- C5 - C4	103.4 (3)	C12	- C13 - C14	94.0 (4)
C2	- C1 - C5	105.1 (3)	C4	- C5 - C6	118.8 (3)	C11	- C14 - C13	85.9 (3)
C1	- C2 - C18	109.7 (3)	C1	- C5 - C6	111.9 (4)	C8	- C14 - C13	121.2 (4)
C1	- C2 - C17	111.0 (4)	C5	- C6 - C7	130.0 (4)	C8	- C14 - C11	117.7 (4)
C1	- C2 - C3	101.9 (3)	C6	- C7 - C8	126.8 (4)	C1	- C15 - N20	179.8 (5)
C17	- C2 - C18	108.3 (4)	C7	- C8 - C14	108.4 (4)	C1	- C16 - N19	175.5 (5)
C3	- C2 - C18	110.3 (4)	C7	- C8 - C9	111.4 (4)	C2	- C17 - N21	178.6 (5)
C3	- C2 - C17	115.5 (3)	C9	- C8 - C14	115.8 (4)	C2	- C18 - N22	179.1 (5)
C2	- C3 - C10	110.2 (3)	C8	- C9 - C10	128.6 (4)			
C2	- C3 - C4	110.8 (3)	C3	- C10 - C9	129.8 (4)			

ACKNOWLEDGEMENT.

Financial support from the Ministero della Pubblica Istruzione is gratefully acknowledged.

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