Tetrahedron Vol. 47, No. 38, pp. 8167-8176, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

β-CYANOCYCLOBUTENONE AS A HIGHLY REACTIVE DIENOPHILE IN COMPARISON TO β-CYANOCYCLOPENTENONE .

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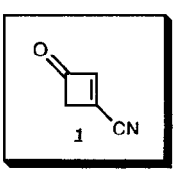
(*Received in Belgium* 11 *July* 1991)

Key words: Cyclobutenone; Cyclopentenone; Diels-Alder; Transition State; PM3 Calculation.

Abstracts: *The thermal [2+2] cycloaddition of α-chloroacrylonitrile to allene followed by ozonolysis, then elimination of HCl provides access to the new β-cyanocyclobutenone* **1** *(Scheme 1) Diels-Alder reactions of* **1** *occur very easily at room temperature The high reactivity of* **1** *in [4+2] cycloadditions strongly contrasts with the low reactivity of the homologous cyanocyclopentenone* **2** *(Scheme 4) This is in agreement with calculations (PM3 method).*

INTRODUCTION

Probably because most cyclobutenones are synthesized from ketenes [1], which prefer electron-rich partners for [2+2] cycloadditions [2], simple cyclobutenones activated by a π electron withdrawing group in position 3 still appear to be unknown. Our study of [2+2] cycloaddition reactions of allenes with captodative olefins [3], has now enabled us to synthesize the first member of this class, the β-cyanocyclobutenone **1** ·



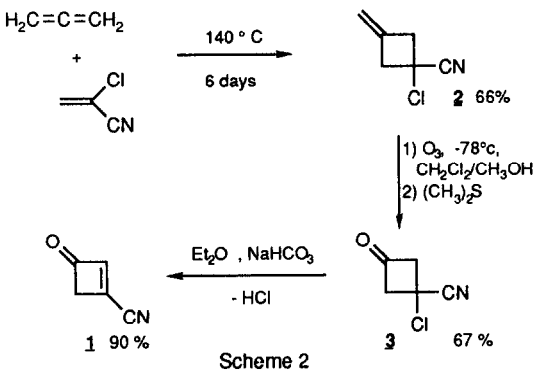
Scheme 1

Five, six and seven membered ring 2-cycloalkenones are known for their very weak dienophilic properties and their Diels-Alder reactions usually require drastic thermal conditions or Lewis acid catalysis [4] Cyclobutenones should be more attractive partners for [4+2] cycloadditions thanks to the relief of angle strain during the reaction However, a recent review about "Diels-Alder reactions of cycloalkenones in organic synthesis" [5] reported only two Diels-Alder reactions of a cyclobutenone : the reactions of 4,4-dimethylcyclobutenone with cyclopentadiene under Lewis acid catalysis and with 1,3 diphenylbenzofuran [6] These two cycloadditions were both carried out at room temperature , presumably to avoid ring opening and vinylketene formation at higher temperature The β-cyanocyclobutenone **1** is found now to be a much better dienophile since the presence of a π electron withdrawing group on the double bond allows faster Diels-Alder reactions at room temperature without catalysis.

EXPERIMENTAL RESULTS

Synthesis of β-cyanocyclobutenone 1

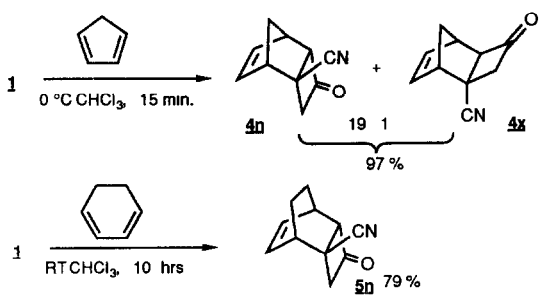
During our study of thermal [2+2] cycloadditions of captodatively substituted olefins with allenes [3], we also examined the reactivity of α-chloroacrylonitrile for comparison. Although, this olefin is less reactive than α-alkoxy or thioalkyl acrylonitriles, it gives 66 % of 3-chloro-3-cyanomethylenecyclobutane **2** [3,7] (Scheme 2). The exocyclic double bond of methylenecyclobutanes can be cleaved to give the corresponding cyclobutanones [8]. Ozonolysis of the exocyclic double bond of **2** affords the unstable 3-chloro-3-cyanocyclobutanone **3** which eliminates HCl very easily Thus transformation to **1** is completed by contact with a weak base like sodium bicarbonate. **1** is very sensitive to bases and heat.

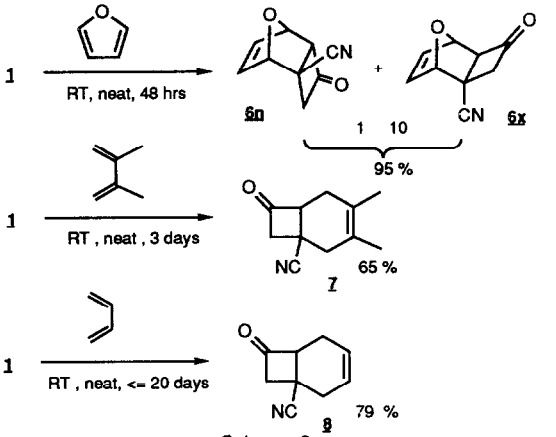


Scheme 2

Reactions of β-cyanocyclobutenone 1

The dienophilicity of the cyclobutenone **1** is demonstrated by [4+2] cycloadditions with five dienes of decreasing reactivity (Scheme 3).



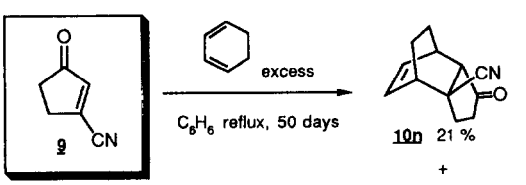


Scheme 3

It is essential to note that all Diels-Alder reactions of the cyclobutenone **1** take place at room temperature, which is necessary in order to avoid vinylketene formation by cycloreversion [9].

[4+2] cycloaddition of β-cyanocyclopentenone 9

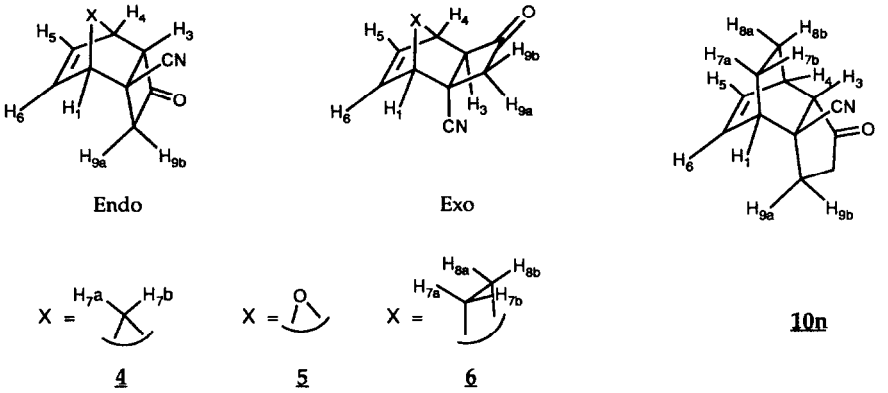
In contrast to the high reactivity of **1**, the homologous cyanocyclopentenone **9** [10] did not react with cyclopentadiene, 1,3-cyclohexadiene, and furan at room temperature. No other Diels-Alder reactions are found in the litterature β-Cyanocyclopentenone **9** is stable at 80 °C and upon refluxing in benzene, reaction occurs extremely slowly with cyclohexadiene to afford the [4+2] cycloadduct in low yield



Scheme 4

Identification of the endo and exo cycloadducts

The stereo structures of the new [4+2] bicycloadducts depicted in schemes 3 and 4 were determined by ^{1}H NMR spectroscopy (Scheme 5 and Table 1)



Scheme 5

Table 1 : selected ^{1}H NMR data.

Endo	Exo	Endo	Exo
4n X = CH_2	**4x**	**6n** X = O	**6x**
$^3J_{3,4}$ = 5.4	$^3J_{3,4}$ = 1 6	$^3J_{3,4}$ = 6 1	$^3J_{3,4}$ < 0 3
$^4J_{7a,3}$ = < 0 6	$^4J_{7a,3}$ = 1 9		
δ H_3 = 4 24	δ H_3 = 3 56	δ H_3 = 4 30	δ H_3 = 3 74
δ $H_{5,6}$ = 6 26	δ $H_{5,6}$ = 6 40, 6 54	δ $H_{5,6}$ = 6 50	δ $H_{5,6}$ = 6 59 , 6,79
δ $H_{9a,9b}$= 2 60, 3 20	δ $H_{9a,9b}$ = 2 85 , 3 30	δ $H_{9a,9b}$ = 2 65 , 3 19	δ $H_{9a,9b}$= 2 97 , 3 27
δ $H_{7a,7b}$= 1 91, 1 99	δ $H_{7a,7b}$= 1 66,1 62		
5n X = CH_2CH_2	**5x**	**10n** X = CH_2CH_2	**10x**
$^3J_{3,4}$ = 3 4			
δ H_3 = 3 76	no exo	δ H_3 = 2 66	no exo
δ $H_{5,6}$= 6 28		δ $H_{5,6}$= 6,20, 6 25	
δ $H_{9a,9b}$ = 2 9, 3 4			
δ bridge 1 45 (3H), and 2 04(1H)		δ bridge 1 35, 1.40, 1 67 and 2 11	

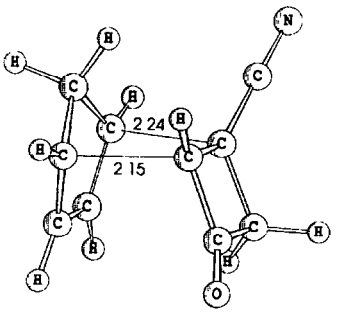
The endo cycloadducts **4n**, **5n** and **6n** show vicinal coupling constants $^3J_{3\text{-}4}$ = 3.4 to 6.1 Hz whereas this value for **4x** and **6x** is 1 6 and less than 0.6 Hz respectively. The W coupling constant [11] $^4J_{3\text{-}7a}$ is 1.9 for **4x** and less than 0 6 Hz for **4n**

The C-C double bond shields the hydrogen H_{9a} in cycloaducts **4n** and **6n** whereas the same double bond shields H_3 in **4x** and **6x**.. The olefinic hydrogens (H_5 and H_6) in **4x** and **6x** are deshielded by the nitrile placed in the endo position whereas in the exo position, the nitrile has a deshielding effect on the methylene bridge of **4n** relative to **4x** Also, one hydrogen of the CH_2CH_2 bridge of the cycloadducts **5n** and **10n** (H7b) is facing the exo cyano group and is deshielded. In the case of the similar endo [4+2]cycloadduct of the non cyano substituted cyclopentenone , for which ^{1}H NMR data has been previously reported [12], there is no particularly deshielded hydrogen on the CH_2CH_2 bridge.

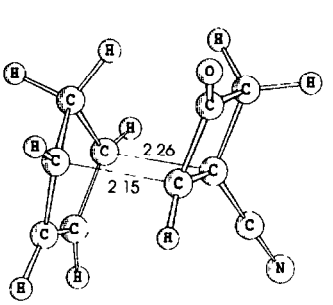
CALCULATIONS

The surprising difference in reactivity between β-cyanocyclobutenone **1** and β-cyanocyclopentenone **2** prompted a MO-theoretical analysis. The PM3 parametrization of the MNDO method[13] was applied to the calculation of the $\Delta H°_f$ values of ground states of starting materials, products, and to the transition structures for the [4+2] cycloadditions of cyclopentadiene with both dienophiles. For β-cyanocyclobutenone both the endo and the exo mode of addition were considered, whereas for the 5-membered ring only the endo addition was evaluated. All structures are geometry optimized, the transition structures are associated with one negative eigenvalue in the Hessian matrix. In Table 2 relevant heats of formation are collected.

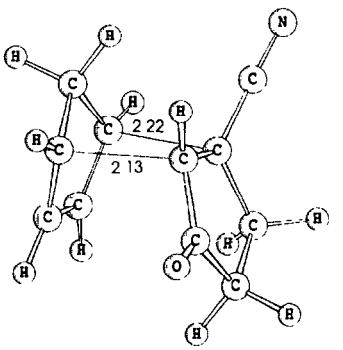
The analysis of the reactivity difference is based on the activation enthalpies which follow from the sum of the heat of formation of the starting molecules and its difference to the heat of formation of the transition structure It is assumed that a possible difference in the activation entropies is negligible, the reactivity pattern thus being enthalpy determined. The $\Delta\Delta H°_f$ values are as follows : endo addition of cyclopentadiene to β-cyanocyclobutenone (transition structure I) 32.2 kcal/mol, the corresponding exo addition (transition structure II) 32 8 kcal/mol, endo addition of cyclopentadiene to β-cyanocyclopentenone (transition structure III) 36.8 kcal/mol. The conclusion is that the reaction of the 4-ring compound requires 4.6 kcal/mol less activation enthalpy in the experimentally preferred endo addition. That means its reactivity is more than 1000 times higher than that of the 5-membered ring compound. Even though the exact difference is not known from the experimental results the observed trend corresponds to the expectation Similarly, the preference for the endo approach, i.e the four-membered ring in endo arrangement of the bicyclo[2.2.1]heptene skeleton **I** , is correctly reproduced, the $\Delta\Delta H°_f$ value of 0.6 kcal/mol being, however, less than required for the experimentally observed ratio of 95.5.



Transition structure I



Transition structure II



Transition structure III

Table 2 : $\Delta H°_f$ values for ground states, transition structures, and products (kcal/mol).

structure	$\Delta H°_f$
cyclopentadiene	31.8
β-cyanocyclobutenone	47.3
β-cyanocyclopentenone	10.1
cycloadduct cyclopentadiene + β-cyanocyclobutenone (exo)	47 5
cycloadduct cyclopentadiene + β-cyanocyclobutenone (endo)	48.7
cycloadduct cyclopentadiene + β-cyanocyclopentenone	25.3
transition structure I	111 3
transition structure II	111 9
transition structure III	78.7

How can we rationalize these results ? Pictures of the transition structures for the endo addition of both dienophiles are shown in I and III . Their similarity is evident. Both cyclopentadiene and the dienophiles are no longer planar molecules as in their ground states. The methylene bridge of cyclopentadiene is bent away from the side of attack of the olefin. The cyano substituent also moves away from cyclopentadiene. Obviously due to repulsive interactions between the non-reacting centers of the two molecules there is no parallel arrangement of the diene part of cyclopentadiene and the 4-, respectively 5-membered ring of the dienophiles. The distance between the reacting centers are of interest. For [4+2] cycloadditions distances of 2.1 - 2.3 Å are typical for symmetrical reactants, regardless whether ab-initio or semiempirical calculations by the AM1 or PM3 procedures are carried out [14,15]. In the case of unsymmetrical reactants unequal bond formation is predicted, the separations may range from 2.1 Å for one bond to 2.4 Å for the second bond[16] In our case the CC distance between the cyano-substituted carbon atom and the relevant atom of cyclopentadiene is 0 08 and 0.09 Å longer than for the other forming bond Unequal bond formation is reasonable as we are not dealing with symmetrical molecules A simple rationalization could be that this situation is caused by secondary interactions between the carbonyl group of the dienophiles and one carbon atom of the diene. A feature of the transition structure for the reaction of cyclopentadiene with β-cyanocyclopentenone III is that both new bonds are 0.02 Å shorter than in structure I . Thus, the transition state for the reaction of β-cyanocyclopentenone is located later on the reaction coordinate than that for the reaction of β-cyanocyclobutenone. One might give a rationalisation for this observation in terms of the reaction enthalpies. Due to the smaller reaction enthalpy for the cycloaddition of β-cyanocyclopentenone ($\Delta\Delta H°_f$ = 13 8 kcal/mol) a later transition state is expected according to the Hammond postulate. Part of the higher reaction enthalpy for the reaction of β-cyanocyclobutenone might be traced back to the decrease in ring strain in going from the cyclobutene to the cyclobutane structure This difference amounts to 3.5 kcal/mol in the parent hydrocarbons[16].

From an energetic point of view a transition structure is characterized by compensation of attractive and repulsive forces between reactants Before reaching the transition state the repulsive forces dominate, beyond it is the covalent stabilization which outweighs the repulsion. The position of this transition structure with respect to distances of the reacting centers carries information about the reactivity The question to be answered is : Why is the separation smaller in the case of β-cyanocyclopentenone ? The answer must be that smaller attractive forces are present at the

geometry where the compensation of repulsion and attraction occurs for β-cyanocyclobutenone.

Perturbation theory is a procedure which should provide insight into this problem. We applied the perturbation program PERVAL [15,17] to this question. The transition structures were used to analyse the interaction between the reactants. They were cut into two subunits, each corresponding to a reactant in its distorted ground-state structure. With the wave functions of these individual molecules we evaluated their interaction in an arrangement corresponding to the transition structure. Even though the perturbation at this point must be rather severe, experience has shown [17,18,19] that such a procedure leads to interesting insight into the forces which determine the reactivity. The precaution which has to be taken is that these results must be interpreted on a semiquantitative rather than on an absolute basis. It is the trend analysis which must provide the explanation, not the interpretation of absolute numbers

The PERVAL calculation is in agreement with the full evaluation of the transition structures : The interaction between β–cyanocyclobutenone and cyclopentadiene in I is 3.0 kcal/mol less repulsive than that between β–cyanocyclopentenone and cyclopentadiene in III (Table 3). The polar interaction between the reactants is in both cases very similar. A discrimination becomes apparent in the closed shell repulsion and the covalent stabilization. Transition structure III displays ca. 5.0 kcal/mol more repulsion, but also ca. 2.0 kcal/mol more attractive forces than I , providing in this way the total difference of three kcal/mol At the transition structures the dominating $HOMO_{diene}$-$LUMO_{dienophile}$ interactions are almost identical in both cases, a small difference in favour of III is observed for the second FMO interaction. Thus it might be argued that a FMO interaction of the observed magnitude is required to reach the transition state in both cases. Due to the differing distances between the reacting centers this occurs for I at separations of the reaction centers which are greater by 0.025 Å. In other words, if the separations were identical for both structures, I should be favored over III by the covalent stabilization. This situation was simulated (entries in line 3 of Table 3). The result is indeed such that now the closed shell repulsion is almost identical for both structures (I and III). The covalent stabilization favors I over III by 1 6 kcal/mol, the main part of which derives from the $HOMO_{diene}$-$LUMO_{dienophile}$ interaction This is now 2.2 kcal/mol more favourable for I than for II. Thus, it may be stated that at a point along the reaction coordinate where the closed shell repulsion is identical, the frontier molecular orbital interaction favors the β-cyanocyclobutenone This results from a lower energy of the LUMO of β–cyanocyclobutenone. This analysis demonstrates that meaningful perturbation calculations require the knowledge of the transition structures as close as possible.

In conclusion it can be stated that the MO-theoretical analysis provides a reasonable explanation of the reactivity difference between the two dienophiles

Table 3 : Perturbation Energies according to PERVAL (PM3 parametrization) (kcal/mol)

Structure	Charge interaction	non-covalent repulsion	covalent stabilisation	sum pertub energies	$HOMO_{diene}$ - $LUMO_{olef.}$	$HOMO_{olef.}$ - $LUMO_{diene}$
I	-4.4	56 4	-39 6	12.3	-22.4	-5 4
III	-4.8	61 6	-41 5	15.3	-22 3	-6.0
III[a)]	-4.5	56.9	-38.0	14.4	-20.2	-5 5

a) Distances between reacting centers in III were elongated by 0 025 Å

ACKNOWLEDGMENTS

We thank Dr Ch. Wynants and Dr. Z. Janousek for valuable discussions as well as the "Institut pour l'encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture" (IRSIA) and the "Service pour la Programmation de la Politique Scientifique" (SPPS) for the financial support.

EXPERIMENTAL SECTION

The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL200, Gemini-200, or Bruker AM500 spectrometer. The samples were dissolved in $CDCL_3$ with TMS as internal standard. The following abbreviations are used : S, s : singlet; D, d : doublet; T, t triplet; Q, q : quartet; m : multiplet, bs : broad singlet. IR and mass spectra were recorded on a Perkin Elmer 1710 and Varian 44SEI apparatus respectively. The UV spectrum of **1** was recorded on a Varian CARY 210 spectrometer. Melting points were determined on a Dr. Tottolli apparatus and are uncorrected.

Synthesis of 3-chloro-3-cyano-1-methylenecyclobutane 2

α-chloroacrylonitrile (5 mmol, 437.5 mg) and a few crystals of hydroquinone are introduced in a 100 ml strong glass tube that can be sealed The tube is then connected to a vessel containing liquid allene (75 mmol, 3 .0 g), cooled at -78°C and allene is transfered into it. After sealing in liquid nitrogen and under vacuum, the glass tube is inserted into a larger protecting metal tube and the whole is heated during 6 days at 140 °C in an oil bath behind a safety shield. CAUTION . the glass tube may explode if not properly sealed ! A metal pressure vessel may be used instead of a glass tube. The tube is cooled in liquid nitrogen and opened. Excess of allene is left to evaporate under hood. The crude product is transferred into a flask and the glass tube is rinsed with chloroform. The solution is filtered and distiled (50 °C / 12 mm Hg) to afford 420 mg (66% yield) of the desired product.

Spectral properties of **2** :

^1H NMR · δ = 3 38 (2H, J = 16.8), 3.68 (2H, J = 16.8), 5.08(2H) AA'BB'XX' system.

^{13}C NMR δ = 47.7 (S,m), 49.4 (T,m, J=143.5), 110 9(T,quint., J=159.3; 3.3), 118 9(S,m), 135 3(S,m)

I R ($CHCl_3$, cm^{-1}) 3090-2940, 2245, 1685

mass spectrum for C_6H_6ClN 129, 127(M^+), 102, 100, 92,89, 87, 40.

Synthesis of 1-chloro-3-oxocyclobutane-1-carbonitrile 3

An ozone / oxygen gas mixture is bubbled through a solution of 3 g (23.5 mmol) of 3-chloro-3-cyano-1-methylenecyclobutane **2** and 3 g of methanol in 100 ml of methylene chloride cooled at -78 °C until the blue color of dissolved ozone appears. The slight excess of ozone is then removed by passing a current of pure oxygen until the blue colour completely disappears. Then, 3 g of a freshly distilled sample of dimethylsulfide is added to the solution that is kept at -20°C for two days in the dark. Solvents and the excess of dimethylsulfide are removed under vacuum at 10-20°C in a rotatory evaporator protected from light. The residue is then stirred for 1 hour with a new portion of 0 5 g of dimethysulfide in a flask cooled at 10 °C and protected from light The excess of dimethylsulfide is removed under vacuum at 10-20°C in a rotatory evaporator protected from light. The residue is poured in 50 ml ether and washed with 12 ml of an ice cold NaCl / HCl solution in order to remove the DMSO formed as byproduct. After drying over $MgSO_4$, the ether is evaporated Recrystallization is done by quickly dissolving at room temperature in a minimun of ether followed by cooling at -20°C. . This is repeated several times and affords 2.04 gr (67%) of colourless crystals The cyclobutanone **3** is not stable and was analysed immediately

Spectral properties of **3**

^1H NMR · δ = 4.0 ppm AA'BB' system

^{13}C NMR δ = 40.4(Sm), 65 5(Tt, 145.5, 2.2), 118.2(Stt 4.7, 2 5), 195.4(Squint , 6 2)

I.R. ($CHCl_3$, cm^{-1}). 3525, 3015, 2920, 2260, 1830, 1700, 1380, 1100, 1030 .

mass spectrum 129(M^+), 102, 101, 94, 89, 87, 66, 42

Synthesis 3-oxocyclobut-1-ene-1-carbonitrile (β-cyanocyclobutenone) 1

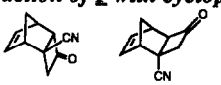
A solution of 680 mgr of 1-chloro-3-oxocyclobutane-1-carbonitrile **3** in 50 ml ether is vigorously stirred with 12 gr of powdered $NaHCO_3$ for 3 hrs in the dark. The salts are filtered and washed with ether. Evaporation of ether at room temperature followed by horizontal distillation (t < 20°C, 0.01 Torr) affords the 3-oxocyclobut-1-ene-1-carbonitrile **1** as a

slightly yellow oil that must be stored in etheral solution in at -20° C. **1** is a lachrymator and it must be each time redistiled before use. Yield : 440 mgr (90 %).

Spectral properties of **1** :

^{1}H NMR : δ = 3.73 (2H, d 0.5), 6.73(1H, t, 0.5)
^{13}C NMR : δ = 53.4(Td, 145.7, 13.5), 111.9(Sm), 139.2(S,t, 7.0), 149.8(Dt ,185.7, 6.2), 184.9(S,m).
I.R. ($CHCl_3$, cm^{-1}): 3030, 2230, 1790, 1555
mass spectrum for C_5H_3NO: 93(M^+), 64, 42.
U V. (CH_3CN, nm) : λ = 236 (log(ε) = 3.9) , 344 (log(ε) = 0.8).

Reaction of 1 with cyclopentadiene



500 mg of 3-oxocyclobut-1-ene-1-carbonitrile **1** is added dropwise to a solution of 1 g of freshly distiled cyclopentadiene in 5 g of $CHCl_3$ cooled at 0 °C The mixture is stirred at 0 °C during 15 min and evaporated The colourless crystalline residue may contain a small amount of cyclopentadiene dimer. It is purified by column chromatography on silica gel with petroleum ether/ethyl acetate 8 : 2 A mixture of endo/exo (19:1) isomers is obtained with a yield of 830 mg (97 %) (mp of the mixture > 80°C).

Spectral properties of the endo isomer :

^{1}H NMR : δ = 1.91 (1H dtt , 9.4 , 1.6, 0.6), 1.99(1H dm 9 4), 2.6 (1H dd 18.4, 3.2 hz), 3 2(1H dd 18.4, 3 2), 3 33(1H m), 3.43(1H m), 4.24(1H, dt , 5.4, 3 2,), 6.24(1H dd , 5.7, 3.0), 6.28(1H dd 5 7, 3.0) .
^{13}C NMR . δ = 28.8(Sm), 45.9(Dm ~150hz), 49.0(Dm ~150 hz), 50.6(DDd, 142.1, 136 4, 0.9 hz), 53.5(DDt 139.0, 134.1, 4.0 hz), 74.4(Dm 149.0 hz), 123.0(Stt, 2 8, 5.6), 131.4(Dm, 173.8), 137.6(Dm 173.2), 202.1(Sm).

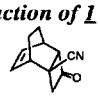
Spectral properties of the exo isomer :

^{1}H NMR : δ = 1.62(1H dm 10.4), 1.66 (1H dqd, 10 4, 1.9, 0.6) , 2.85(1H dd 18.6, 3.0), 3.30(1H dd 18.6, 3.5, note : the values 3.30 ppm and 18.6 Hz are deduced because of the overlapping of the signals of the major endo isomer), 3.25(1H m), 3.37(1H m), 3 56(1H ddddd 3 5, 3 0, 1 9, 1.7, 0.4), 6 40(1H dd 5 7, 3 1), 6.54(1H, 5 7, 3 1)
^{13}C NMR : δ = 32.0, 41 4, 43 4, 48.1, 48 7, 73 5, 122 2, 137.5, 138.2, 202 9

Spectral properties of the mixture of isomers .

I R ($CHCl_3$, cm^{-1}): 3000, 2240, 1790, 1385, 1335
mass spectrum (EI) for $C_{10}H_9NO$: 159(M^{+}), 158, 131, 130, 117, 116, 103, 91, 79, 66.

Reaction of 1 with cyclohexa-1,3-diene

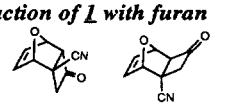


500 mg of 3-oxocyclobut-1-ene-1-carbonitrile **1** and 516 mg (1.2 eq) of cyclohexa-1,3-diene are stirred in 15 ml of $CHCl_3$ during 10 h at room temperature. After evaporation of the solvent, the residue is purified by column chromatography on silica gel with $CHCl_3$. Yield : 735 mg (79%) mp 171°C.

Spectral properties of the endo isomer :

^{1}H NMR : δ = 1.3 - 1.5 (3H m), 2.0(1H m), 2.9(1H dd 18.4, 3.4), 3.0(1H m), 3.1(1H m), 3.4 (1H dd 18.4, 3 4), 3.76(1H q 3.4), 6.28(2H m)
^{13}C NMR : δ = 20.2 (Tm 132.8), 21.8(Tm 132.8), 27.2(Sm), 30.3(Dm 143.0), 34.0(Dm 140.4), 55.6(T 138.6), 70.5(Dm 143.2), 122.6(Sm), 129.6(Dm 168.4), 133.8(Dm 167.6), 203.1(Sm).
I.R. ($CHCl_3$, cm^{-1}) : 3010, 2960, 2880, 2240, 1800, 1380.
mass spectrum (EI): 173(M+), 145, 131, 130, 117, 116, 104, 103, 91, 77, 77, 68, 58
Anal. calc. for $C_{11}H_{11}NO$. C 76.28, H 6.40, N 8.09 ; found : C 76.30, H 6.38, N 8.10

Reaction of 1 with furan



A solution of 500 mg of 3-oxocyclobut-1-ene-1-carbonitrile **1** (5 38 mmol) in freshly distiled furan is left to stand for 2 days at room temperature. Part of the product crystallises in the flask. Excess of furan is evaporated and ^{1}H NMR analysis is performed on the residue in order to measure the endo/exo ratio The residue is purified by column chromatography on silica gel with petroleum ether/ethyl acetate 7 . 3 (rf = 0.15(endo) and 0.22(exo)) and affords 130 mg of pure exo isomer plus 690 mg of a mixture of both isomers. Total yield : 95%. Endo/exo ratio 1/10. The exo isomer decomposes at 144 °C .

Spectral properties of the exo isomer

^{1}H NMR : δ = 2.97(1H dd 18 1, 2 7), 3.27(1H dd 18.1, 3.2), 3.74(1H d 3.2, 2.7), 5.26 - 5 32 (2H m), 6 59(1H dd 5.8 1.7), 6.79(1H dd 5.8 1.7).
^{13}C NMR . δ = 32.2(Sm), 48.1(DDm, 141.7, 138.9), 73 2(Dm, 153.5), 80.2(Dq 170.7, 10.3), 82.2(Dm, 170.3), 119 9(Sm), 136 2(Dt, 179 7, 3 4), 137 3(Dt 180 1, 3 9), 199 1(Sm)
I R ($CHCl_3$, cm^{-1}) 3020, 2240, 1800, 1380, 1320

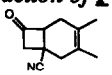
Spectral properties of the endo isomer

^{1}H NMR δ = 2.65(1H dd 18 6, 3 1), 3 19(1H dd 18.6, 2.9), 4.39(1H, dt, 6 1, 3.0), 5 41(1H bs), 6 5(1H bs) The signals for the other bridgehead and the other olefinic hydrogens overlap with the corresponding signals for the major exo isomer

Spectral properties of the mixture of isomers ·

mass spectrum (EI): 161(M^{+}), 160, 143, 133, 119, 104, 93, 91, 81, 68, 64, 51, 39
Anal. calc for $C_9H_7NO_2$ C 67 08, H 4.38, N 8.69 ; found 67 12, H 4.40, N 8 73

Reaction of 1 with 2,3-dimethylbutadiene



A solution of 730 mg (7.85 mmol) of 3-oxocyclobut-1-ene-1-carbonitrile **1** in 2 g of 2,3-dimethylbutadiene stabilized with 0.1% of hydroquinone is left to stand at room temperature for three days. Colourless crystals precipitate and are filtered (380 mg, mp : 64°C). The filtrate is evaporated and the residue (910 mg) is purified by column chromatography on silica gel with petroleum ether/ethyl acetate 8 : 2 (rf = 0.32). Total yield : 900 mg (65%). Degradation occurs in contact with the air.

Spectral properties

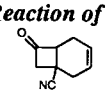
^{1}H NMR : δ = 1.70 (3H m), 1.76 (3H m), 2.25 - 2.28 (2H, bs), 2.44(1H dbs 3.8), 2.65(1H, dm 3.3), 2.89(1H ddd 18.1, 2.9, 0.4), 3.60(1H dd 18.1, 3.8), 3.88(1H m).

^{13}C NMR : δ = 19.2(Q 126.5), 19.6(Qd 126.8, 3.3), 25.0(Sm), 28.5(Tm 130.9), 36.4(Tm 130.8), 56.3(Tm 138.5), 64.3(Dm, 140.4), 123.3(Sm), 123.4(Sm), 128.2(Sm), 205.2(S sext, 6.4).

I.R. ($CHCl_3$, cm^{-1}) : 2920, 2220, 1790, 1445, 1380.

mass spectrum (EI) : 176, 175(M^+), 132, 133, 118

Reaction of 1 with butadiene



500 mg of 3-oxocyclobut-1-ene-1-carbonitrile **1** (5.38 mmol) is placed in a glass tube with 2.3 g of condensed butadiene together with a few crystals of hydroquinone. The mixture is degased and the tube is sealed. After 20 days at room temperature, the glass tube is cooled at -78°C and opened. The excess of butadiene is left to evaporate under the hood. The residue is purified by column chromatography on silica gel with CH_2Cl_2 and affords 624 mg (79% yield) of a colourless liquid.

Spectral properties

^{1}H NMR : δ = 2 06 to 2.73 (4H m), 2.99(1H dd 18.1, 2.7), 3.67(1H dd 18.1, 3 8), 3.92(1H m), 5 93(2H m).

^{13}C NMR . δ = 21.4(T 129), 24.2(S), 29.6(T, 132), 57.0(T 139), 63.5(D 139), 123.4(S), 123.8(D 169), 128.4(D 169), 205.9(S 159).

I.R. ($CHCl_3$, cm^{-1}) : 2220, 1800, 1650.

mass spectrum (EI): 147(M^+), 119, 105, 104, 91, 78, 65, 51, 43.

Reaction of 2 with cyclohexa-1,3-diene

410 mg of 3-oxocyclopent-1-ene-1-carbonitrile **2** (3.8 mmol) and 400 mg of cyclohexa-1,3-diene are dissolved in 10 g. of benzene. The mixture is heated under reflux and after 15 days, a new portion of 450 mg of cyclohexa-1,3-diene is added. 7 days later, another portion of 460 mg of cyclohexa-1,3-diene is added again. Progress of the reaction was monitored by TLC (rf (ether) 3-oxocyclopent-1-ene-1-carbonitrile **2** · 0.77 , product : 0.64). After 50 days, the solvent is evaporated and the residue is purified by column chromatography on silica gel with a variable solvent mixture of ether/petroleum ether. The yield is 150 mg (21%) and 160 mg of **2** (39%) are recovered Mp : 122°C.

Spectral properties :

^{1}H NMR · δ = 1.35(1H dm, 12.1), 1 40(1H dm, 12 9), 1.67(1H, m), 1.94(1H dt 13.4, 9.6), 2.11(1H m), 2.14(1H m), 2.38(1H m), 2.48(1H ddd, 13.4, 10 5, 4 0), 2.67(1H bs), 2.96(1H m), 3.08(1H m) , 6.20(1H ddd 8 2, 6.6, 1 3), 6.25(1H ddd 8.2, 6.5, 1.1).

^{13}C NMR : δ = 21.9(Tm 133), 22.9(Tm 132), 31.7(Tm 135), 31.9(Dm 143), 36.9(Tm 130), 37.8(Dm 141), 41.5(Sm), 57.5(Dm 138), 125.0(Sq ~6hz), 131 8(Dm 168), 134.6(Dm 167.5), 215.8(Sm).

IR (KBr) : 2966, 2943, 2227, 1743, 1270, 1231, 1190.

mass spectrum (EI): 187(M^+), 144, 130, 117, 109, 104, 103, 91, 80, 79, 77, 65, 56, 51.

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