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Products of the Anionic Oligomerization of the Pure 1-Cyclohexene-1-carbonitrile and of Its Mixtures with the 3-Cyclohexene-1-carbonitrile Isomer

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SUMMARY

Noncyclic unsaturated dimers and trimers are the principal products in the $KOC(CH_3)_3$ catalyzed oligomerization of the pure 1-cyclohexene, 1-carbonitrile, and of its mixtures with the 3-cyclohexene-1-carbonitrile isomer.

Pure isomeric dimers such as the cis and trans 1-(2'cyanocyclohexyl)-cyclohex 3-ene-carbonitrile were isolated from the raw reaction mixtures. Their configurations and conformations were investigated by IR and NMR.

Possible mechanisms of the oligo- and cooligo- merization are proposed.

INTRODUCTION

In recent years Shnalke et al. (1976) isolated a cyclic trimer such as the 1,3,9-tricyanoperhydrophenylene from the reaction mixture of the oligomerization of the 1-cyclohexene-1-carbonitrile (I) in the presence of strong bases (yields being 50% with NH_3 / $LiNH_2$, 30% with $(Me)_2SO$ / $NaNH_2$, and 20% with DMSO / $KOC(CH_3)_3$.

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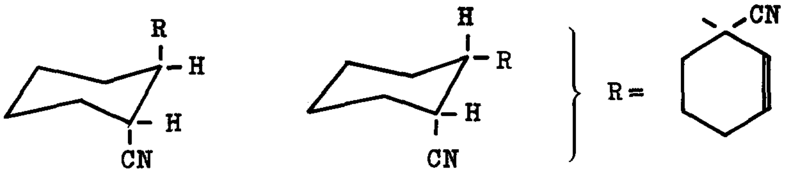
From the polymerization products of (I), on the contrary, in presence of $KOC(CH_3)_3$, with and without solvents, we succeeded in the separation of two cis/trans isomeric noncyclic unsaturated dimers with fairly good yields (40-60%).

Their structures must be consistent with the following formula :



The other reaction products mainly derive from the above reaction are simply trimers and tetramers of I.

From the polymerization of the 1 : 1 mixture of (I) with the 3-cyclohexene-1-carbonitrile isomer (II) the trans 1-(2'cyanocyclohexyl)-cyclohex-3-ene-carbonitrile was, on the contrary, isolated.

EXPERIMENTAL

The 3-cyclohexene-1-carbonitrile was prepared by a well established procedure which involves a Diels-Alder reaction of the butadiene with acrylonitrile (Van Caille 1933). The 1-cyclohexene-1-carbonitrile was, on the contrary, synthesized by high temperature isomerization of the above Δ^3 isomer, using iron pentacarbonyl as a catalyst (Messina et al. 1979).

Experiments were carried out in a magnetically stirred glass vessel. The nitrile was added dropwise to the catalyst solution (DMSO and ether as solvent) and allowed to react for the desired time at temperature from 20 to 60°C.

The reaction is highly exothermic and, to avoid overheating, needs to be cooled. To keep **rigorously** the temperature at 15 ÷ 20°C, a procedure was devised which permits a dropwise addition of the nitrile into a fine suspension of the catalyst in anhydrous ether, with a contemporaneous stirring and cooling of the reaction mixture.

The raw reaction products were washed with water, extracted with ether and after evaporation of the ether, distilled under high vacuum.

GPC analysis of the reaction mixtures were performed with a Waters instrument Model LC 201, using a μ-Styragel 10^2 Å column.

NMR Spectra were run at 60 MHz in $CDCl_3$ and CS_2 solution with Jeol, JNM-C-60HL, spectrometer. Low and high temperature Spectra were done with the JES-UT-3 temperature controller.

RESULTS

From I two reaction mixtures were obtained: one (A) working without solvent and the other (B) with solvent, namely DMSO.

A GPC study of A and B is consistent with a molecular distribution as shown below :

	PM average	Monomer	Dimer	Trimer	Tetramer
A	280	14	36	25	25
B	270	7	45	48	-

One of the reaction mixtures was fractionated under high vacuum conditions (ca. 10^{-5} mmHg). The fraction collected at 130°C and 2×10^{-5} mmHg, after crystallization from the ether solution, gave a white crystal product, 1, (40% : m.p. = 108-110°C). A viscous liquid, 2 (60%), was, on the contrary, separated by evaporation of the ether solvent. Both products, observed by IR, showed two distinct bands in the spectral range 2214 ÷ 2216 cm^{-1}, evidence of the existance of two different -CN groups.

From a mixture of I and II (1:1 ratio) a reaction mixture was obtained, that, under high vacuum distillation, gave a fraction (ca. 10% at 145-155°C and 3×10^{-5} mm Hg : crystallization from the ether solution of this fraction gave a white crystal product, 3, (ca. 30% : m.p. = 125-127°C). Evaporation of the ether solution leaves a viscous liquid that, analyzed by G.C., appeared to be a very complex mixture of several unidentified products.

The IR spectrum of 3 showed a single -CN stretching band. 1, 2 and 3 were then carefully analyzed by NMR in order to state their configurations and conformations. Their 60 MHz Spectra in $CDCl_3$ are shown in Figs. 1, 2, and 3. The spectra and the relative intensities of the bands are in agreement with

Fig. 1

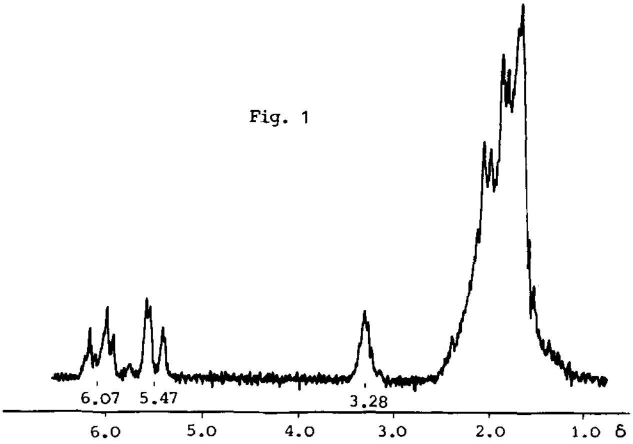


Fig. 2

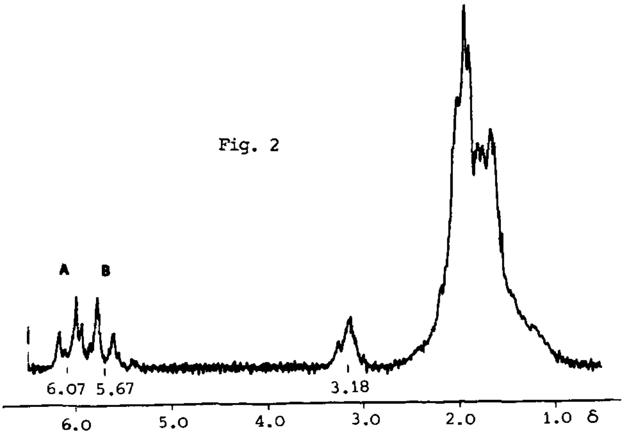
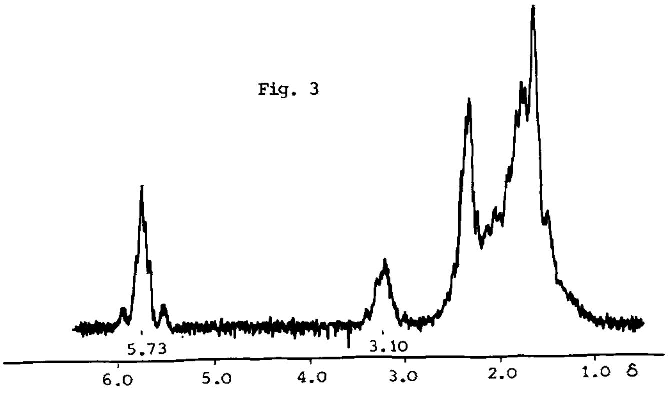
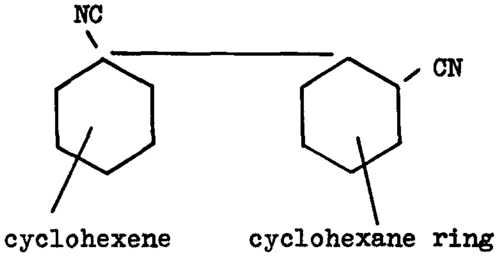


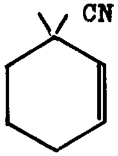
Fig. 3



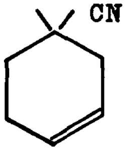
the following basic structure :



valid for all three molecules in question. The two olefinic protons have a NMR pattern quite similar in 1 and 2 : an AB quartet with the A part uncoupled with other vicinal protons and the B part coupled with a $-CH_2-$ vicinal group. 3 , on the contrary, gives a single broad band for the two olefinic protons, evidence of their near chemical equivalence. These patterns can be confidentely related to the double bond position in the cyclohexene ring, namely :



for 1 and 2



for 3

That, in addition, justifies the two CN IR bands for 1 and 2, one for the -CN on the saturated ring and the other for the -CN with the double bond of the cyclohexene ring in the β-γ position. The $>C\underline{H}\,C\,N$ signal is the absorption with more diagnostic value. The chemical shifts (Hz from TMS) and the half-widths (Hz) of this band are shown below :

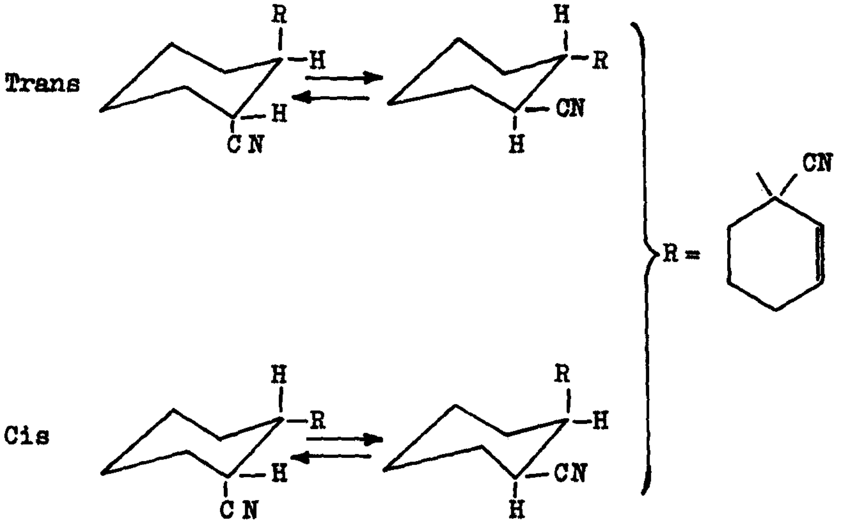
	$\underline{1}$	$\underline{2}$	$\underline{3}$
$>C\underline{H}\,C\,N$	197	186	191
$\Delta^{\frac{1}{2}}$	ca. 7	ca. 7	ca. 10

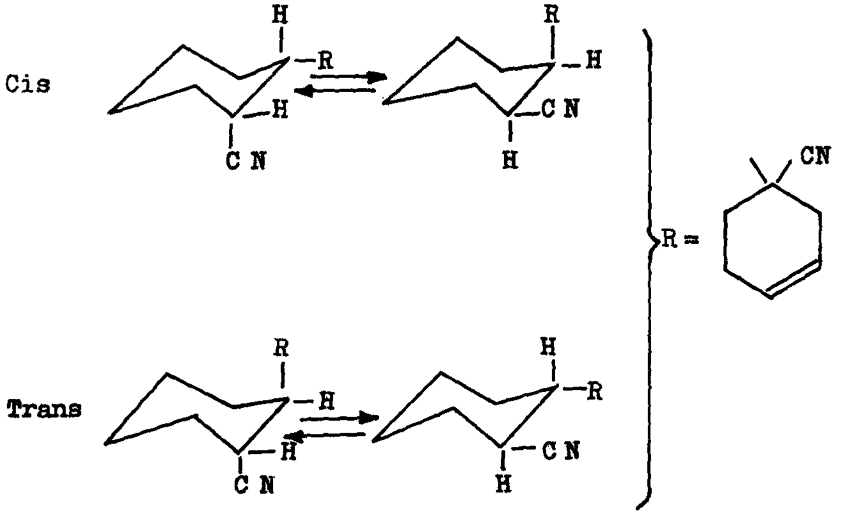
The half-width values of this signal is rather low. This means that the $>C\underline{H}\,C\,N$ proton must have a predominant equatorial position. This consideration comes from the well established rule (H. Booth 1969) that in saturated six-membered ring $J_{ee} \simeq J_{ea}$ (ca. 4 Hz) J_{aa} (ca. 9 Hz). For our three molecules in question, to justify the small half-width observed for $>C\underline{H}\,C\,N$, the proton has to be involved only in couplings of the type J_{ee} and J_{ea} and not of the J_{aa} type. Some spectra at different temperatures (+100 $\underline{+}$ -100°C), using solvents such as exachlorobutadiene and CS_2, were also run with the purpose to see whether some conformational changes could be evidentiated. The $>CH\,C\,N$ bands do not show any appreciable change either in chemical shift or in half-width. This is a clear evidence that the molecules must exist predominantely in only one conformation.

If we write down the different structures with their possible conformations, Table 1, on the basis of the

Table 1 : Possible structure for 1 , 2 and 3

R / CN





experimental evidences before indicated, only conformations with $>C\underline{H}CN$ protons in equatorial position can be thought possible. On the basis of $>C\underline{H}CN$ chemical shifts, taking in account the anisotropic contribution of the cyclohexene double bonds as it appears looking at the Dreiding models, one can eventually and tentatively make the following assignments:

$\underline{1}$ to Trans - structure

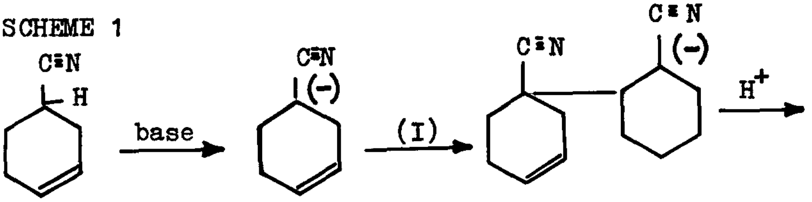
$\underline{2}$ to Cis - structure

$\underline{3}$ to Trans - structure

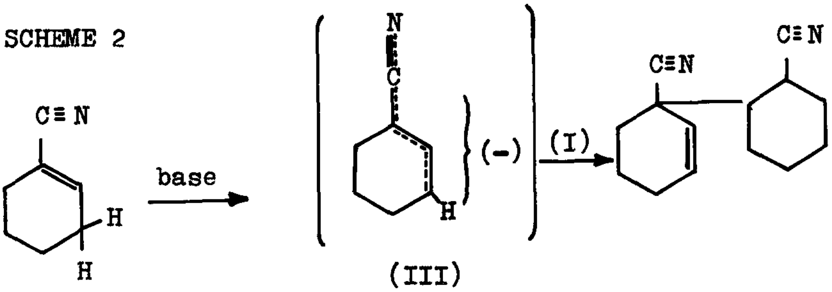
POLYMERIZATION MECHANISM

From the structures of the dimers that appears during polymerization either for the pure I or for the I/II mixture the initiating species must be a carbanion with the negative charge centered in α to the -CN group. However, while in the case of the codimer $\underline{3}$, such an anionic center can be directly generated over the Δ^3 cyanocyclohexene (scheme 1), this cannot be the case in the polimerization of the pure Δ^1 isomer : here, a mechanism pathway such the one of scheme 2, can be reasonably assumed : this resembles the well established pathway of the alkylation with alkyl halides of α, β unsaturated acids, esters and ketones, from which, in basic medium, the α-alkyl-β,γ -unsaturated derivatives are formed (Yanovskaya and Shakhidayatov 1970). Consequentely the initiating species is likely to be the highly stabilized anion (III), originated by the attack of the strong base on the allylic hydrogens situated in position 3 to the -CN group.

SCHEME 1



SCHEME 2



REFERENCES

MESSINA G. et al. : La Chimica e l'Industria, in press (1979)

SHNALKE K.E. et al. : c.a. 85; 46265y (1976)

VAN CAILLE. R. : Bull, Soc. Chim. Belg. 42 - 419 (1933)

YANOVSKAYA L.A. and SHAKHIDAYATOV Kh. : Russ. Chemical Reviews 39, 865 (1970)

BOOTH H. : Progress in NMR Spectroscopy, V5, p. 149, Pergamon P., 1962

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