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PALLADIUM-PROMOTED FORMATION OF CYCLOHEXENONITRILES FROM 1-HEXENE AND ACRYLONITRILE

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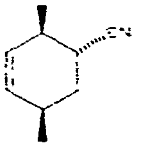
Summary

Acrylonitrile and 1-hexene react in the presence of palladium on charcoal to give four isomers of 3,6-dimethylcyclohexenonitriles along with 2,5-dimethylbenzonitrile. The reaction probably involves palladium-promoted dehydrogenation of 1-hexene to 2,4-hexadienes followed by a Diels—Alder reaction between 2,4-hexadiene and acrylonitrile. The structures of the main products are discussed.

During studies of acid-catalyzed ene reactions we investigated palladium chloride-promoted addition of 1-hexene to acrylonitrile. Instead of the anticipated ene adduct, small amounts of a mixture of the compounds I—V were formed together with palladium metal. The adducts are obviously derived from 2,4-hexadiene and acrylonitrile. Palladium(0) on carcoal was found to be a superior catalyst for the reaction, giving total yields based on acrylonitrile of the order of 30%. The reaction, which proceeds at moderate rate at 140°C, probably involves dehydrogenation of 1-hexene to a mixture of *Z,E*- and *E,E*-2,4-hexadiene, followed by a Diels—Alder-reaction with acrylonitrile.



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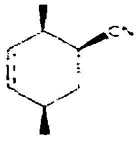

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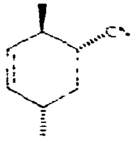

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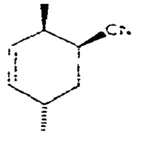

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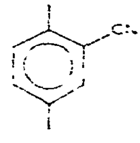
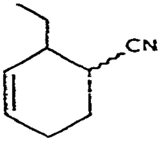


(V)

Dehydrogenation of 1-hexene to hexadienes has been observed earlier, but temperatures above 200°C have generally been employed. In addition, rather complex mixtures were obtained [1,2]. Since no free hydrogen is evolved under our conditions, the excess of 1-hexene probably acts as hydrogen acceptor. No adducts VI derived from 1,3-hexadiene were identified. This is in contrast to the related addition of 1-hexene to quinone which yields diethylanthraquinone VII [3].



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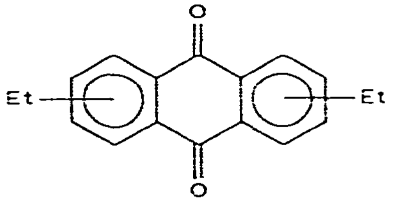

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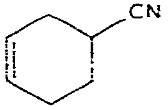
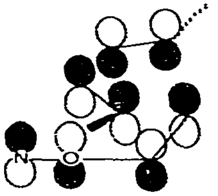


(VIII)

The major products I, II, and V were isolated by preparative GLC. The structure of compound V was determined by comparison with an authentic sample. The overall structures of I and II were determined from NMR, mass spectra, dehydrogenation to the aromatic nitrile V, and by synthesis of a mixture of I and II from acrylonitrile and *E*,*E*-2,4-hexadiene; the configurations were then deduced from chemical and NMR data. The structures of the minor compounds III and IV were inferred from their mass spectra and from dehydrogenation experiments.

Acrylonitrile also reacted with 1-butene to yield 3-cyclohexenocarbonitrile (VIII) in a very low yield. Methyl acrylate gave adducts with 1-hexene similar to those obtained with acrylonitrile, but the yields were much lower.

The Diels—Alder reaction between acrylonitrile and *E*,*E*-hexadiene gave mainly two isomers in a ratio 1.2 : 1. Due to secondary interactions, *endo* addition is generally preferred in reactions between dienes and acrylates. The major isomer is thus expected to be the *cis* isomer II, formed via the *endo* transition state IX.



(IX)

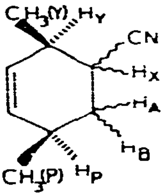
In the reaction between cyclopentadiene and acrylate, Lewis acids have been observed to increase the *endo* selectivity [4,5]. This is probably due to an increase of the orbital coefficient at the carbonyl carbon, leading to increased secondary overlap with the π-system of the diene [6]. Similarly, Lewis acids would be expected to increase the yield of the all *cis* isomer II from *E*,*E*-2,4-hexadiene and acrylonitrile. In accord with this assumption, the II : I ratio was found to increase from 1.2 : 1 to 11 : 1 on addition of aluminum chloride. It was also found that the major isomer II was dehydrogenated to dimethylbenzonitrile (V) much more rapidly than the isomer I by the action of dichlorodicyanobenzoquinone (DDQ). Since overlap between the π-systems of DDQ and the Diels—Alder adducts should be more facile with the isomer II, this result is also in accordance with the assigned structures. Finally, an extensive NMR study allowed the assignment of the coupling constants J_{xy} for the isomers I and II.

TABLE 1

CHEMICAL SHIFTS (δ, ppm) AND COUPLING CONSTANTS J(Hz) OF THE ALIPHATIC PROTONS OF ISOMERS I AND II

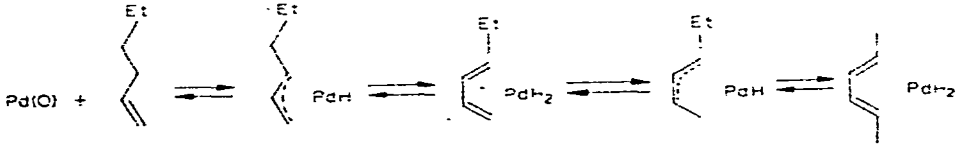
	I	II		I	II
δ(A)	1.97	1.46	J(AB)	−13.2	−12.5
δ(B)	1.71	1.92	J(AP)	6.0	9.5
δ(X)	2.2-2.5	2.79	J(AX)	9.7	11.5
δ(P)	2.2-2.5	2.0-2.5	J(BP)	5.0	5.5
δ(Y)	2.2-2.5	2.0-2.5	J(BX)	2.4	3.0
δ(CH$_3$(P))	1.02	1.04	J(XY)	8.0	5.3
δ(CH$_3$(Y))	1.15	1.16	J(CH$_3$(Y)Y)	6.5	7.5
			J(CH$_3$(P)P)	7.0	7.0

The coupling constant was smaller (5.3 Hz) for the major isomer II than for I (8 Hz), again in accordance with the assigned structures.



Since the NMR spectra of compounds I and II were complex, unequivocal assignment of shifts and coupling constants is not possible. However, with the aid of a shift reagent, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium, Eu(fod)$_3$, tentative assignments can be made. Since one of the methyl groups is shifted more than the other in both isomers, this must be the group *ortho* to the nitrile group. In the same way the *x* proton can be identified. The *y* proton undergoes the second largest shift and can be identified by the coupling to the *y* methyl group. This makes possible a determination of the coupling constant J_{xy}, which should be the most characteristic difference in the NMR spectra of the two isomers. The coupling constant J_{xy} is larger for the isomer I (8 Hz vs. 5.3 Hz) in agreement with the assignments based on chemical evidence. Also the fact that the NMR signals are more strongly shifted for the isomer I is in accordance with the assigned stereochemistry. From the shifted NMR spectra and a study of isomer I at 270 MHz it has been possible to determine the shifts and coupling constants of the aliphatic protons of the isomers I and II (Table 1). Only the determination of which is which of the A and B protons remains uncertain.

The dehydrogenation reaction of 1-hexene and 1-butene may proceed via the π-allyl complex X. This is of obvious interest in connection with other reactions of π-allylpalladium complexes, e.g. nucleophilic addition [7]. In fact, preliminary experiments show that low yields of amination products may be detected under dehydrogenation conditions if amines are present [8].



(X)

Experimental

For analytical gas chromatography, 5% FFAP on Chromosorb W was used as stationary phase and for preparative gas chromatography 10% polyethylene glycol on Chromosorb W.

Reaction of 1-hexene with acrylonitrile and Pd/C

20 ml 1-hexene, 5 ml acrylonitrile and 0.9 g Pd/C were heated in a sealed tube in a rocking furnace at 140°C for 24 h. The catalyst was filtered off, and excess 1-hexene and acrylonitrile were evaporated. The residue was then bulb-to-bulb distilled. Yield 3.2 g. The distillate was analyzed by gas chromatography (GC). Five products were formed in the ratios 48 : 37 : 6 : 3 : 6. The two major products were shown to be the dimethylcyclohexenonitriles II and I, respectively. The last product was the aromatic derivative V. The other two products could not be isolated in sufficient amounts to determine their structures. Since their mass spectra were very similar to those of the compounds I and II, their structures most probably are III and IV.

Dehydrogenation of the hexenonitriles I and II

A mixture of I and II was reacted with DDQ in refluxing toluene for 24 h. GC-analysis of the crude reaction mixture showed that 20% of the compound I and 70% of the compound II had been consumed. After dilution with light petrol to precipitate the major part of the hydroquinone, the solution was filtered through an alumina column and the dehydrogenation product isolated by preparative GC. It was identical to an authentic sample of 2,5-dimethyl benzonitrile (IR, MS, NMR, GC).

Diels—Alder reactions between E,E-2,4-hexadiene and acrylonitrile

(a) Uncatalyzed reaction. 1 ml 2,4-hexadiene and 5 ml acrylonitrile were heated in the presence of about 20 mg hydroquinone in a sealed tube at 100°C for 6 h. GC analysis of the mixture revealed the existence of two isomers at the same retention times as I and II. These isomers were isolated by preparative GC, and were identical (GC, MS, NMR) to the products from the palladium-catalyzed reaction. The ratio I : II was in this case 45 : 55. The yield was about 40%, but was not optimized.

(b) Catalyzed reaction. If one equivalent of $AlCl_3$ based upon hexadiene is added, the stereospecificity is considerably increased. After 24 h at 60°C the ratio I : II is 13 : 87 and after 26 h at room temperature the ratio is 8.5 : 91.5.

NMR studies

The appropriate nitrile (I or II) was dissolved in $CDCl_3$, and the NMR spectrum was recorded at several concentrations of added $Eu(fod)_3$. The results are shown in Table 1. According to these results, the most probable structures are II for the major compound and I for the next largest.

Acknowledgements

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