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REACTIONS OF ORGANIC ANIONS. XII. VINYLATION OF PHENYLACETONITRILE DERIVATIVES

M. Mąkosza
Department of Organic Technology II,
Institute of Technology /Politechnika/, Warsaw 10, Poland

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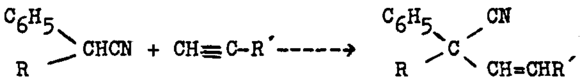
The direct O-, S-, and N-vinylation, an important reaction, proceeds in the presence of basic catalysts, and is usually considered as a nucleophilic addition to the acetylenic bond /1/. However, only a few examples of direct C-vinylation are known. Karpukhin /2/ prepared 9-vinylfluorene from fluorene and acetylene at 200° under 30 atm. in the presence of NaOH. Seefelder /3/ vinylated ethyl alkylmalonates with acetylene at 150-180° under 15 atm. The addition of dimethyl sulphoxide anion to diphenylacetylene /4/ as well as some examples of the intramolecular addition of carbanions to the acetylenic bonds occurring during malonic ester alkylation with pentyne tosylate /5/ or with some vinylacetylene bromides /6/ are also reported. The free radical C-vinylation was reported to proceed with poor yields /7/.

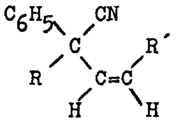
We found that the anions of alkylarylacetonitriles react with acetylene under mild conditions to give vinyl derivatives. For example, when a mixture of 2-phenylbutyronitrile, NaOH, some DMSO, and triethylbenzylammonium chloride was saturated with acetylene, an exotermic reaction took place yielding of 2-vinyl-2-phenylbutyronitrile /I/ /equation 1, R'=H/, b. 118°/16 mm Hg, n_D^{20} 1.5170, yield 80%. I hydrogenated on Pt gave known 2-ethyl-2-phenylbutyronitrile; hydrolysis of I yielded 2-vinyl-2-phenylbutyric acid m.p. 67° which, in turn, on hydrogenation gave the known 2-ethyl-2-phenylbutyric acid, m.p. 93°. I treated with bromine gave 2-ethyl-2-phenyl-3,4-dibromobutyronitrile, b. 123°/0.1 mm Hg, n_D^{20} 1.5738. Other phenylalkylacetonitriles behave similarly, their reactivity decreasing with the chain length increase.

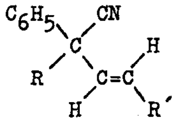


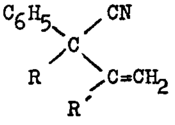
R'= H, I

R'= C_6H_5, II

The addition of nitriles to phenylacetylene proceeds still easier /equation 1, R'=C_6H_5/. Three isomers are here possible:


IIa


IIb


IIc

In the majority of cases /depending on R/ II was isolated by vacuum distilation as on oily substance. When R=iso-C_3H_7 the distilled product was semi-solid and on filtration and crystallization gave cis isomer /IIa/, m.p. 63°.

When R=$C_6H_5CH_2$ the main product obtained was crystalline /m.p. 147°/ and possessed the cis configuration. The residue was a cis - trans mixture from which a product m. 117-120° was isolated. This was the trans isomer contaminated with approx. 20% of the cis form. There was no evidence of the IIc formation.

Configurations of olefinic nitriles were established by NMR. The structure assignments was based on the coupling constants of the AB system vinyl protons. The values observed were 11.8 and 16.5 cps for the cis and trans isomers, respectively. This is in agreement with the generally known higher values for trans structures /8/.

Table 1 shows the data concerning the physical properties and yields of some olefinic nitriles prepared by this method.

TABLE 1

Yields and Physical Properties of Olefinic Nitriles I and II

No.	R	R′	Yield /%/	b.p.	n_D^{20}
1	CH_3	H	83	110/8	1.5158
2	C_2H_5	H	80	118/16	1.5170
3	iso-C_3H_7	H	82	120/8	1.5163
4	C_5H_{11}	H	88	139/8	1.5066
5	C_2H_5	C_6H_5	94	134/0.7	1.5807
6	iso-C_3H_7	C_6H_5	83	145/0.8	1.5782 m.p. 62° [x]
7	$C_6H_5CH_2$	C_6H_5	98		m.p. 147° [x]
8	$/C_2H_5/_2NCH_2CH_2$	C_6H_5	79	152/0.2	1.5712

[x] Data for pure cis isomer. Satisfactory analyses have been obtained for all compounds.

We found also that in the condition applied the addition of alkylarylacetonitriles to diphenylacetylene and 1-hexyne did not take place. Similarly, there was no reaction with diphenylacetonitrile. Presumably, low activity of diphenylacetonitrile anion, as compared with phenylalkyl one /9/, plays a decisive role in the described case.

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