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α-CARBON PARTICIPATION IN ELECTROLYTIC HYDRODIMERIZATION

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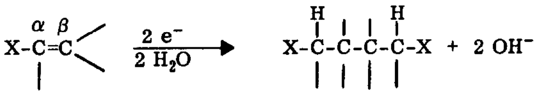
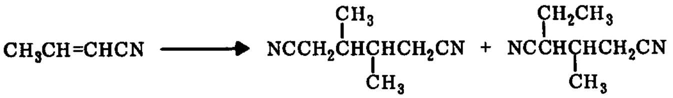
It has been indicated (1, 2, 3) that the electrolytic hydrodimerization of activated olefins results in coupling through the β-position. We have found that the dimerizations of crotononitrile and methacrylonitrile involve the participation of the α-carbon as well as the β-carbon. Although the dimerization



in which X = -CN, -COOR, -CONR$_2$, etc.

occurs largely through the β-position, small amounts of dimers also arise through the α-position.

The dimerization of crotononitrile results mainly in 3,4-dimethylhexanedinitrile (2), but a very small amount (less than one area percent of dimers by gas chromatographic analysis) of 2-ethyl-3-methylglutaronitrile (A) is also produced. The 2-ethyl-3-methylglutaronitrile (A) was isolated by gas



$$CH_3CH{=}CHCN \longrightarrow NCCH_2\overset{CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_2CN + NCC\overset{CH_2CH_3}{\overset{|}{H}}\underset{CH_3}{\underset{|}{C}}HCH_2CN$$

A

chromatography and then identified by its nuclear magnetic resonance, mass, and infrared spectra. The NMR spectrum[1] (CDCl$_3$) was studied at both 60 and 100 Mc. and was found to be consistent with structure A. The three protons of the methyl on the ethyl group appear as a triplet centered at 1.09 p.p.m. (J ~ 7 cps.). The three protons of the second methyl group appear as a pair of doublets centered at 1.18 and 1.20 p.p.m. (J ~ 7 cps.), thus indicating the material to be a mixture of isomers. The two protons of the methylene of the ethyl group appear as a multiplet centered at 1.54 p.p.m. The single proton on C-3 appears as a multiplet centered at 2.14 p.p.m. The three protons on C-2 and C-4 appear as a multiplet from 2.43 to 2.75 p.p.m. The areas for the absorptions were in excellent agreement with

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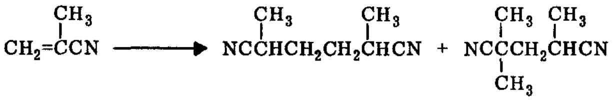
[1] NMR spectra were recorded on Varian A-60 and HA-100 instruments. Field position values are referred to tetramethylsilane as an internal standard.

the theoretical areas. The mass spectrum was found to have fragment peaks at m/e 68, 69, 96, 54, 41, 121, 94, and 39 (in order of decreasing intensity). This spectrum was compared with that of 3,4-dimethylhexanedinitrile and was found consistent with structure A.

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.5; H, 8.9; N, 20.6. Found: C, 70.5; H, 9.1; N, 20.7.

The dimerization of methacrylonitrile mainly results in a mixture of isomers of 2,5-dimethylhexanedinitrile, but a small amount (8 to 11 area percent of dimers by gas chromatographic analysis) of 2,2,4-trimethylglutaronitrile (B) is also formed. This material (B) was isolated by gas chromatography and its structure proven by its nuclear magnetic resonance and infrared spectra. The NMR



$$CH_2{=}\overset{CH_3}{C}CN \longrightarrow NC\overset{CH_3}{C}HCH_2CH_2\overset{CH_3}{C}HCN + NC\underset{CH_3}{\overset{CH_3}{C}}CH_2\overset{CH_3}{C}HCN$$

B

spectrum (60 Mc., $CDCl_3$): CH_3CH, doublet, 1.41 p.p.m., J ~ 7 cps. (3H); CH_3C, singlet, 1.41 p.p.m., (3H); CH_3C, singlet, 1.47 p.p.m. (3H); HCH, pair of doublets, 1.79 p.p.m., J = 14.2 cps. and J = 5.7 cps. (1H), pair of doublets, 1.89 p.p.m., J = 14.2 cps. and J = 8.0 cps., (1H); CH, sextet, 2.90 p.p.m., (1H).

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.5; H, 8.9; N, 20.6. Found: C, 70.1; H, 8.8; N, 20.2.

These products arise by a reaction involving the addition of an α-carbon intermediate, perhaps a carbanion, to the conjugate system of a second molecule.

ACKNOWLEDGMENT

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