

Further Studies of the Interaction of Carbonyl Compounds with Organometallic Azides, the Reaction of Acrylonitrile with Trimethylsilyl Azide

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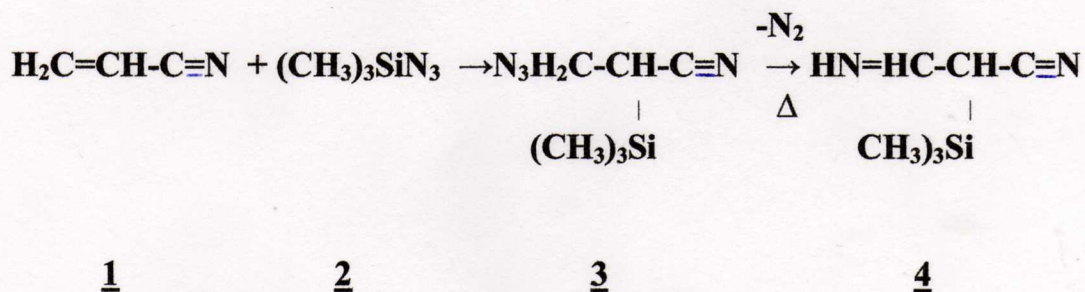
Report of Investigators to the National Cancer Institute, 1973

Abstract:

Acrylonitrile (1) on reaction with trimethylsilyl azide (2) gave complex mixtures, with 3-imino-2-trimethylsilyl propionitrile (4) being the major isolatable product in low yield. The reaction was slow even in high boiling solvents due to the electron withdrawing cyano group decreasing the nucleophilicity of the conjugated double bond. Considerable intractable polymer was always produced. The mechanism is believed to involve anti-Markonikov 1,2 addition of trimethylsilyl azide (2) to the double bond of 1, giving intermediate 3-azido-2-trimethylsilyl propionitrile (3). Loss of nitrogen gives imine (4). See plate 1. The mechanism is supported by the detection of an intermediate believed to be 3 on g.c. analysis, which rapidly disappeared giving 4. The reaction is of limited synthetic utility due to the slow rate and tendency of acrylonitrile to polymerize even with inert solvent added as diluent.

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PLATE 1



Experimental:

Reaction of Acrylonitrile (1) with Trimethylsilyl Azide (2)

To a 50 ml 3 neck round bottom flask was charged 5.3 g (0.10 mol) acrylonitrile, with stirring, into 20 ml heptane. The solution was heated to 100° and charged with 14 ml (0.010 mol) trimethylsilyl azide. Heating was continued under nitrogen and the mixture periodically analyzed by GC (6 ft SE30 column, 120°). After 4 days reflux GC showed 2 new peaks, plus unreacted acrylonitrile and trimethylsilylazide. On continued heating one of the new peaks disappeared with concurrent growth of a higher boiling second peak. A precipitate was also produced. After 7 days reflux all acrylonitrile and trimethylsilyl azide had disappeared on GC analysis. The mixture was cooled, and a brown solid was filtered from the solution. It failed to melt and was insoluble in all solvents, indicative of polymer. The heptane was stripped from the liquid product and the high boiling oil distilled under pump vacuum, yielding 3-imino-2-trimethylsilylpropionitrile (4) b.p., 95° (0.05 mm). Wt 1.6g (11%).

I.R. (film), 3300 (broad, NH), 3060(w), 2960(m), 2240 (s, nitrile), 1610,(s, NH), 1420(m), 1360(w), 1280(s), 1250(s), 1135(s), 1050 (w), 955(s), 875(s), 755 (m), 695 (m) cm^{-1} .

UV (extinction coefficient) (heptane), 252(9000) mu.

PMR (100Mhz, CCl_4 , benzene internal standard), δ 6.52 (1H, J= 8 Hz, olefinic), 5.30 (broad, 1H, N-H), 3.84 (1H, J= 8 Hz, de shielded aliphatic), 0.13 (9H, trimethylsilyl).

Anal. Calc. For $\text{C}_6\text{H}_{12}\text{N}_2\text{Si}$:

C, 51.38, H, 8.62, N, 19.98.

Found: C, 51.20, H, 7.72, N, 20.12. Satisfactory.