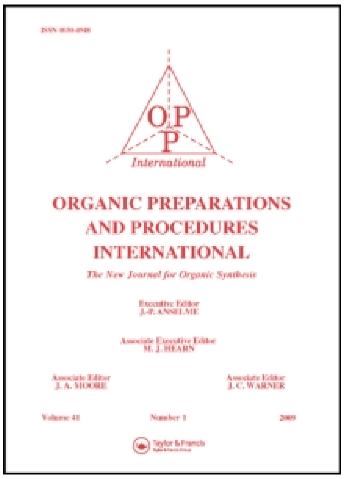

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2,2-'AZOBIS(2-CYANO-*n*-PROPANOL). A NEW FREE RADICAL INITIATOR

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2,2'-AZOBIS(2-CYANO-n-PROPANOL). A NEW FREE RADICAL INITIATOR

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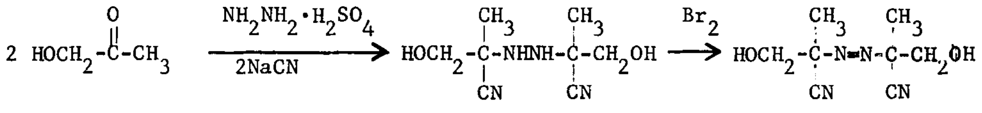

$$2\ HOCH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[2NaCN]{NH_2NH_2\cdot H_2SO_4} HOCH_2-\underset{CN}{\overset{CH_3}{C}}-NHNH-\underset{CN}{\overset{CH_3}{C}}-CH_2OH \xrightarrow{Br_2} HOCH_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_2OH$$

I II III

Simple azo initiators containing reactive functional groups are rare. Those derived from levulinic acid[1] and 5-hydroxypentane-2-one[2,3] are known. The synthesis of the simplest member of the hydroxy family, 2,2'-azobis(2-cyano-n-propanol) (III), prepared by the Strecker synthesis, is now reported here using readily available acetol (I).

The procedure of Overberger, Huang and Berenbaum[4] was used with some modification. Compound III was obtained in two different soluble forms. Yields of recovered products did not exceed 60%. By the use of 100% excess hydrazine sulfate and sodium cyanide in a conventional one pot, flask reaction gave after bromine oxidation of II, a 50% yield of the high melting isomer (Isomer I)[5] without ether extraction of the aqueous wash liquids. Loss in yield is minimized by keeping the volume of wash water to a minimum.

The hydrazo compound II could be obtained as a thick orange oil in 74% crude yield from the orange colored solution by liquid-liquid extraction with ether for 4 days. Although a few crystals could be observed, no pure product could be obtained even after column chromatography. An attempt to distill a small amount at 0.75 mm, (head temperature of 52°) failed. Further purification efforts were not attempted. The infrared spectrum (neat) of this oil exhibited the following bands: 3300 (broad), 2970 s, 2930, 2870, 2225 (C≡N), 1650, 1435 (CH_2) 1370 (CH_3), 1250, 1075, 1050 (CH_2OH), 850 cm^{-1}.

EXPERIMENTAL[6]

2,2'-Azobis(2-cyano-n-propanol) (III) - A 900 ml. ordinary bottle cooled in ice water was charged with 31.2 g. (0.24 mole) of hydrazine sulfate, 600 ml. of ice water, 33.3 g. (0.45 mole) of acetol[7] (I), and 24.5 g. (0.5 mole) sodium cyanide. The bottle was capped with a Poly-Seal cap and rolled on a jar mill for 20 hrs. All reactants had dissolved after 5 min. The bottle was cooled again in ice water and 7 ml. of 6N HCl was added and the mixture allowed to stand for 24 hrs. The bottle was cooled to 10° in ice water, a stirring magnet added, and bromine 75 g. (0.47 mole) was added over a period of 6 hrs. A precipitate started to form after 2 ml. of bromine had been added. The excess bromine was destroyed by sifting in 12 g. of sodium bisulfite with stirring. The suspension was filtered and the cake washed with small amounts of ice water until the filtrate gave no precipitate with silver nitrate. The cream powder was dried under vacuum to give 14.7 g. (33%) of compound (III), mp. 124-125.5°(dec.) as the high melting isomer (Isomer I)[5]. Recrystallization from THF or benzene-THF gave a fine powder composed of small flakes.

Recrystallization from chloroform gave colorless plates mp.129.5° (dec. clear melt). IR (KBr) 3455 (O-H), 2250 ($C\equiv N$), 2940, 2880, 1255, 1060 cm^{-1}; UV (MeOH) 345 (ε 12.6), 255 mμ (ε 3190); nmr δ (CD_3-$COCD_3$) 1.61 (s, 6H), 4.00 (m, 4H), 4.80 (t, 2H, J=6Hz).

Anal. Calcd for $C_8H_{12}N_4O_2$: C, 48.98; H, 6.17; N, 28.56.
Found: C, 48.70; H, 6.19; N, 28.60.

The combined light yellow aqueous solution (filtrate and washings, 1.5 l.) was placed in a 2 l. liquid-liquid extractor with 2 pounds of 3 mm glass beads and extracted with 200 ml. ether for 24 hrs[8]. After this time, a crystalline precipitate had formed in the solvent reservoir. The receiver was changed and the extraction repeated for 48 hrs. with fresh ether. The first ethereal extract on cooling gave 9.86 g., mp. 108-111.5°(dec.) of the low melting isomer (Isomer II). The second extract on concentration and cooling gave 0.25 g. of the high melting isomer and further concentration gave 0.71 g. of the low melting isomer. The total yield of III was 25.52 g. (58%).

Recrystallization of isomer II from ether gave colorless octahedral crystals, whereas recrystallization from benzene-THF (2:1) gave well defined hexagonal prisms mp. 109.5°(dec.). IR (KBr) 3320 (O-H), 2240 ($C\equiv N$), 2990, 2935, 1055, 1040 cm^{-1}; UV (MeOH) 345(ε 14.2), 260mμ (ε 1640); nmr δ (CD_3COCD_3) 1.68 (s, 6H), 3.96 (m, 4H), 4.82 (t, 2H, J=6Hz).

Anal. Calcd for $C_8H_{12}N_4O_2$: C, 48.98; H, 6.17; N, 28.56.
Found: C, 49.31; H, 6.11; N, 28.63

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5. This isomer is tentatively assigned the meso form; the low melting isomer (Isomer II) is then the ± isomer.
6. Melting points were taken in a Hershberg oil bath and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 621, ultraviolet spectra were obtained on a Cary 14, and nmr spectra were measured with a Varian A-60. Elemental analyses were performed by Galbraith Laboratories, Inc., and MH&W Laboratories, Garden City, Mich.
7. Jefferson Chemical Co., Houston, Texas, redistilled bp 59°/29 mm, n_D24 1.4208.
8. Column chromatography of the residue obtained by evaporation of solvent on silica gel using tetrahydrofuran removes the yellow color from impure ± isomer, whereas alumina gave only a degraded oil.

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