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PARTIAL HYDROLYSIS OF ADIPONITRILE AND SEBACONITRILE BY HYDROGEN PEROXIDE

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Of the ω-cyanocarboxamides having six or more carbon atoms, only ω-cyanovaleramide, a derivative of adipic acid, has been prepared and it has not been fully characterized (1, 2). It was prepared from adipic acid in 67% yield (2). In the present study ω-cyanovaleramide and ω-cyanopelargonamide have been prepared by partial hydrolysis of adiponitrile and sebaconitrile with alkaline 3% hydrogen peroxide (3) in 31% and 6% yields respectively. Other methods including alkaline and acid hydrolysis gave lower yields or no cyanoamide at all.

RESULTS AND DISCUSSION

The preferred procedures given in the experimental section for the preparation of ω-cyanovaleramide and ω-cyanopelargonamide were selected after a study of time, temperature, and ratio of reactants as process variables. They are procedures which give the best yields obtained and are at reasonable conversions.[2] As usual in such partial reactions, it is necessary to balance conversion against yield. Higher conversions than those associated with the maximum yields gave lower yields of cyanoamide. Thus, in a run at 52% conversion, 25% yield of ω-cyanovaleramide was obtained and at 89% conversion, 9% yield. Experiments with adiponitrile showed that of the factors examined, the temperature at which the peroxide is added to the dinitrile and the ratio of hydrogen peroxide to dinitrile were the most important factors controlling yields. Increase in temperature during addition increased both yield of amide and conversion over the range −10° to 70° with optimum yields of 24.6% and 89% conversion at 70°. An increase in the ratio of hydrogen peroxide to dinitrile is associated with a two-fold increase in the yield of amide at 5° but at 35–40° a similar change in ratio of reactants results in a decreased yield of amide. The result is that the maximum yield of amide was obtained at 5°. Conditions which gave a 31% yield of cyanovaleramide from adiponitrile gave only 1.8% yield of cyanopelargonamide from sebaconitrile. An increase in the temperature to 40° gave the best yields observed under any conditions, 6%. Further increase in temperature gave no increase in yield. It is possible that an extended study of these variables may disclose more favorable conditions for preparative procedures for these cyanoamides.

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[2] Conversions are determined on the basis of recovered dinitrile. Thus, if one mole of dinitrile were reacted and 0.5 mole of unchanged dinitrile recovered, conversion is calculated on the basis of the 0.5 mole of dinitrile that has reacted. If 0.25 mole of cyanoamide were formed, the yield for this hypothetical case would be 25%; the conversion 50%.

EXPERIMENTAL PART

ω-Cyanovaleramide. A solution prepared by adding 2 g. of potassium hydroxide dissolved in 2 ml. of water to 130 ml. of fresh 3% hydrogen peroxide is placed in a 500-ml. three-necked round-bottom flask fitted with an efficient stirrer, a dropping-funnel, and a thermometer. Acetone (20 ml.) is then added to the flask which is immersed in an ice-bath and the contents cooled to 3–5°. A solution of 27 g. (0.25 mole) of adiponitrile[3] dissolved in 20 ml. of acetone is added dropwise over a one-hour period to the reaction mixture with stirring and at 3°. The mixture is then refluxed one-half hour on the steam-bath.

The acetone is removed on a steam-bath under a slight vacuum. The residue, if acid, is made alkaline with potassium hydroxide and saturated with sodium chloride, and continuously extracted with ethyl acetate for 24 hours. The extracts are filtered to remove any precipitated diamide. The ethyl acetate is removed under reduced pressure, and the residue, which consists of unreacted adiponitrile and the cyanoamide, is distilled rapidly from a Claisen flask, using a metal bath which has been pre-heated to 250°. As soon as all of the adiponitrile, b.p. 169–171° at 25–26 mm., has been removed the temperature rises rapidly and the distillation is stopped when a solid appears in the condenser. The residue is impure ω-cyanovaleramide, m.p. 62–64°. Recrystallization from a mixture of acetone and ethyl ether gives 9.8 g. of a white solid, m.p. 66–67°, conversion 43%, yield 31%.

Anal. Calc'd for $C_6H_{10}N_2O$: C, 57.12; H, 7.99; N, 22.21.
Found: C, 57.07; H, 8.14; N, 22.00.

ω-Cyanopelargonamide. A solution of 63.8 g. (0.39 mole) of sebaconitrile (4), b.p. 151–155° at 4–5 mm., in 50 ml. of acetone, is placed in the reaction vessel equipped as above. A solution prepared from 200 ml. of 3% hydrogen peroxide to which has been added 4 g. of potassium hydroxide dissolved in 4 ml. of water and 50 ml. of acetone is added dropwise through the separatory-funnel over a one-hour period while the temperature of the reaction mixture is 40–45°. The ω-cyanopelargonamide is then isolated following the procedure used above. The crude material is recrystallized from a mixture of ethyl ether and petroleum ether to give 4.2 g. of a white solid, m.p. 74–75°, conversion 12%, yield 6%. A mixture melting point using a sample prepared by treating ω-cyanopelargonic acid with thionyl chloride and ammonium hydroxide gave no depression.

Anal. Calc'd for $C_{10}H_{18}N_2O$: C, 65.89; H, 9.95; N, 15.37; M.W., 182.
Found: C, 66.21; H, 10.60; N, 15.19; M.W., 189 (Method of Rast).

SUMMARY

ω-Cyanovaleramide has been characterized and the previously unknown ω-cyanopelargonamide has been prepared, isolated, and characterized. A study of the variables in the partial hydrolysis of adiponitrile and sebaconitrile to the corresponding cyanocarboxamides has been made and preferred conditions for isolation of the cyanoamides have been described.

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REFERENCES

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(3) Radziszewski, *Ber.*, **18**, 355 (1885).
(4) Biggs and Bishop, *Org. Syntheses*, **25**, 95 (1945); D'Alelio and Reid, U.S. Patent 2,019,941 (1938).

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[3] The authors are indebted to the DuPont Company for graciously supplying the adiponitrile used in this study.