liter at 25°. Ultraviolet absorption E_{max} in 2% aqueous dimethylformamide 16500 at 366.0 mμ.

Anal. Calcd. for $C_9H_9N_3O_5$: C, 45.19; H, 3.79; N, 17.57. Found: C, 45.13; H, 3.80; N, 17.33.

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The Hydrolytic Rearrangement of α-Cyanoisopropyl Mesitoate[1]

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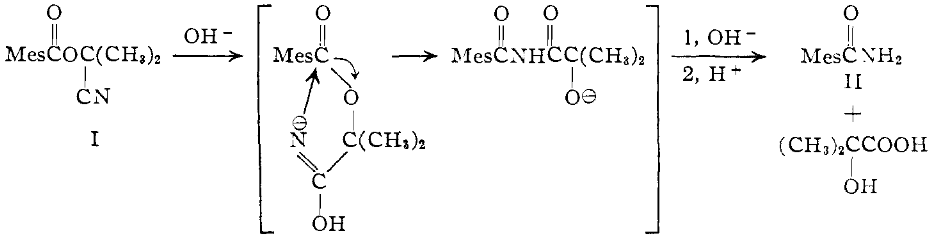
In connection with other work, the action of ethanolic sodium hydroxide on α-cyanoisopropyl mesitoate (I) has been examined. From this reaction, mesitamide (II) and α-hydroxyisobutyric acid were isolated. It is suggested that this reaction involves an intramolecular rearrangement which probably proceeds in the manner



Mes = 2,4,6-trimethylphenyl

Steric hindrance around the ester carbonyl group prevents attack of the hydroxide ion at that site so that the less reactive but unhindered nitrile function is attacked. Attack of the strongly nucleophilic intermediate imide ion on the carbonyl group is followed by tautomerization to the hydroxy imide which undergoes hydrolysis in the alkaline solution to mesitamide and α-hydroxyisobutyric acid. That the intramolecular rearrangement proceeds faster than simple hydrolysis of the nitrile is not unexpected since it has been demonstrated by Fuson and his co-workers[2,3] that the hindrance offered to intramolecular processes by the *o*-methyl groups is considerably less than to intermolecular processes. For instance, Fuson and Hammann[3] have shown that highly hindered ketones undergo a series of intramolecular ring closures involving the hindered carbonyl function and neighboring groups.

This hydrolytic rearrangement appears to be specific for sterically hindered esters as α-cyanoisopropyl benzoate was hydrolyzed rapidly and quantitatively to benzoic acid. In this case attack by hydroxide ion at the ester carbonyl proceeded normally.

Experimental[4]

α-Cyanoisopropyl Mesitoate.—To 51.0 g. (0.52 mole) of acetone cyanohydrin contained in a 200-ml. flask was added 91.5 g. (0.5 mole) of mesitoyl chloride with stirring. After addition was complete, the mixture was refluxed for two hours and then poured into water. The resulting mixture was extracted with four 100-ml. portions of methylene chloride. The organic extracts were washed with 10% sodium hydroxide solution and water, then dried and concentrated to yield 90.7 g. (79%) of α-cyanoisopropyl mesitoate, m.p. 40–42°. An analytical sample was prepared by distillation, b.p. 135–136° (8 mm.).

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 73.11; H, 7.63; N, 5.56.

Reaction of α-Cyanoisopropyl Mesitoate with Sodium Hydroxide.—A solution of 4.6 g. (0.02 mole) of α-cyanoisopropyl mesitoate in 50 ml. of ethanol was added to a solution of 8.0 g. (0.2 mole) of sodium hydroxide in 50 ml. of ethanol. The resulting mixture was heated under reflux for six hours and then poured into water. The solid that separated was collected on a filter; yield 1.6 g. The filtrate was extracted with ether and upon concentration of these extracts an additional 0.5 g. of solid was obtained. Recrystallization from benzene gave white crystals of mesitamide, m.p. 187–189° (lit. m.p.[5] 189°); total yield 2.1 g. (71%).

The aqueous extracts were acidified and subjected to continuous ether extraction for 18 hours. Upon drying and concentrating the ether solution there was obtained 1.8 g. (86%) of α-hydroxyisobutyric acid, which was identified by comparison of its infrared spectrum with that of an authentic sample.

α-Cyanoisopropyl Benzoate.—To 109.2 g. (0.52 mole) of trifluoroacetic anhydride contained in a 500-ml. 3-neck flask was added 62.2 g. (0.51 mole) of benzoic acid at 0–10°. The resulting mixture was stirred under reflux for 30 minutes. It was then cooled to 10° and 42.5 g. (9.5 mole) of acetone cyanohydrin was added at such a rate that the temperature did not rise above 20°. After the addition was complete the mixture was stirred at room temperature for 30 minutes, and then poured into water and the product isolated by conventional methods. α-Cyanoisopropyl benzoate was isolated by distillation at 0.01 mm. as a white solid, m.p. 37–38°, yield 48.7 g. (52%).

Anal. Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86. Found: C, 69.51; H, 5.16.

Reaction of α-Cyanoisopropyl Benzoate with Sodium Hydroxide.—When 3.8 g. (0.02 mole) of α-cyanoisopropyl benzoate was treated with 8.0 g. of sodium hydroxide in the manner described for the corresponding mesitoate, 2.3 g. (96%) of benzoic acid, m.p. 120–122°, was obtained.

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[1] This work was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] R. C. Fuson, W. D. Emmons and R. Tull, *J. Org. Chem.*, **16**, 648 (1951).

[3] R. C. Fuson and W. C. Hammann, THIS JOURNAL, **74**, 1626 (1952).

[4] We are indebted to Dr. Keith S. McCallum for infrared interpretations and to Miss Annie Smelley for the micro-combustion data.

[5] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. III, p. 84.

Perfluorinated Butadiene

BY A. L. HENNE AND WM. POSTELNECK

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To allow a new, three-step synthesis of perfluorobutadiene,[1] we have treated 1,2,2-trifluoro-1,2-dichloroiodomethane[2,3] with zinc in acetic anhydride

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[1] W. T. Miller, *et al.*, *Ind. Eng. Chem.*, **39**, 401 (1947).

[2] J. T. Barr, *et al.*, THIS JOURNAL, **73**, 1352 (1951).

[3] R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).