of phenanthrenes and pyrenes, 0.10 g. of yellow oil consisting of pyrenes, and 0.13 g. of an orange oil (most strongly adsorbed) consisting of pyrenes. (Analysis of the residual gas by means of the mass spectrometer showed the presence of methane.) The third fraction was refluxed for 75 minutes with 25 ml. of acetic acid and 2.15 g. of sodium dichromate dihydrate, poured into water, taken up in benzene, washed, dried and concentrated to small volume, giving 0.16 g. of yellow crystals, m.p. 229–249°. The mother liquor was chromatographed on silicic acid–celite; separation was very poor. Ultraviolet spectra of the various fractions showed the presence of substituted fluorenones. The material of m.p. 229–249° was shaken with benzene and Claisen alkali; the alkali-soluble material was crystallized from aqueous acetic acid, giving a bright yellow solid, m.p. 249–260° (sintering from 241°). Recrystallization gave 43 mg., m.p. 260–268° (sintering from 250°). *Anal.* Calcd. for methylfluorenonecarboxylic acid, $C_{15}H_{10}O_3$: C, 75.6; H, 4.2. Calcd. for dimethylfluorenonecarboxylic acid, $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 75.8; H, 4.7. One fraction of the chromatogram above (300 mg.) was converted to the oximes by the pyridine method and the solid was crystallized from benzene, giving a few mg. of yellow crystals, m.p. 146–151°. *Anal.* Calcd. for methylfluorenone oxime, $C_{14}H_{11}NO$: C, 80.4; H, 5.3; N, 6.7. Found: C, 79.9; H, 5.7; N, 6.3.

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The Reaction of Acrylonitrile with Alkyl Lactates

By C. E. Rehberg and Marion B. Dixon

Bruson and Riener made an extensive study of the cyanoethylation of alcohols[1] and concluded that almost all primary and secondary alcoholic hydroxyl groups could be cyanoethylated, though no examples of derivatives of α-hydroxy acids were given. In a latter review[2] Bruson stated that "Only the esters of hydroxy acids have resisted cyanoethylation; attempts to add ethyl glycolate, ethyl lactate and ethyl ricinoleate to acrylonitrile have failed." This unexpected result, together with our broad interest in the chemistry of lactic acid, prompted us to attempt to cyanoethylate several hydroxy acid derivatives.

The compounds used were methyl, ethyl and butyl lactate, N,N-dimethyllactamide and isopropyl glycolate. The latter two were unreactive and were recovered unchanged. The lactate esters behaved erratically and results were not readily reproducible. The butyl ester gave best results, and yields of the expected product were usually in the range 50–80%. An unknown by-product derived principally from acrylonitrile was obtained in every experiment with butyl lactate.

Ethyl lactate behaved more erratically than the butyl ester; an unknown by-product was also produced; and separation of this by-product was difficult.

Methyl lactate gave totally unpredictable results; sometimes it was recovered unchanged; other times none was recovered. The product seemed to be a mixture of the expected cyanoethyl ether and another compound having nearly the same boiling point.

Sodium or potassium (dissolved in the lactate) was the only effective catalyst found. Neither solid nor concentrated aqueous potassium hydroxide nor Triton B, Bruson's preferred catalyst, was effective. No significant difference in the effectiveness of sodium and potassium was demonstrated, nor did the amount used (1–4 g. per mole of lactate) appear important.

Experimental

Cyanoethylation of Butyl Lactate.—One gram of sodium or potassium was dissolved in 1.0 mole of butyl lactate, the temperature being kept below 25°. One mole of acrylonitrile was then added slowly, with stirring. If, as the acrylonitrile was added, no heat evolution was noted, the temperature was raised until there was evidence of reaction (usually at 50–75°). The temperature was then kept constant until addition of acrylonitrile was complete. Then either the mixture was left overnight at room temperature or it was heated on a steam-bath for one hour (no significant difference in results). The catalyst was neutralized with acetic acid and the product was distilled in vacuum.

An unknown product distilled at 90° (1.2 mm.) and had $n^{20}{}_D$ 1.4523; $d^{20}{}_4$ 0.9910; sapn. equiv., 195; C, 66.36; H, 6.11; N, 22.58; empirical formula, $C_{18}H_{20}ON_5$.

The cyanoethyl ether of butyl lactate boiled at 55° (0.04 mm.), 77° (0.2 mm.) and 109° (1.0 mm.) and had $n^{20}{}_D$ 1.4333; $d^{20}{}_4$ 1.0038; and *MR*, sapn. equiv., C, H and N, respectively, calcd., 51.42, 199, 60.3, 8.6 and 7.0; and found, 51.60, 195, 60.5, 8.7 and 7.0. Yields, based on lactate used, were usually in the range 50 to 80% and were somewhat improved by the use of a two- or threefold excess of acrylonitrile. Such excess nitrile usually was largely converted into polymer, however.

Cyanoethylation of Ethyl Lactate.—The procedure used was the same as with butyl lactate. Results were less reproducible, however. Yields of the cyanoethyl ether varied unaccountably from 0 to 70%. An unknown by-product boiling slightly below but close to the desired product made purification tedious. A pure sample of this by-product was not obtained. The cyanoethyl ether of ethyl lactate boiled at 95° (1.0 mm.) and had $n^{20}{}_D$ 1.4302; $d^{20}{}_4$ 1.0427; and *MR*, sapn. equiv., C, H and N, respectively, calcd., 42.18, 171, 56.1, 7.7 and 8.2; and found, 42.43, 165, 56.1, 7.7 and 8.4.

Cyanoethylation of Methyl Lactate.—Very erratic results were obtained in seven experiments. It appeared that at least two compounds were produced and that the cyanoethyl ether was contaminated with another material having almost the same boiling point. A pure sample of the expected cyanoethyl ether was not isolated. A somewhat impure sample had b.p. 90° (1.2 mm.); $n^{20}{}_D$ 1.4344; $d^{20}{}_4$ 1.0680; *MR*, calcd., 37.56; found, 38.36; and sapn. equiv., calcd., 157; found, 166.

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[1] H. A. Bruson and T. W. Riener, THIS JOURNAL, **65**, 23 (1943).

[2] H. A. Bruson, "Organic Reactions," Vol. 5, Roger Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 2, p. 89.

[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

Derivatives of 2-Phenylbenzimidazole

By Merrill Rope, Robert W. Isensee and Lionel Joseph[1]

In connection with a systematic study of certain derivatives of benzimidazole, we have prepared all the monochloro-, monobromo- and monoiodo-derivatives of 2-phenylbenzimidazole. The monobromo and monoiodo derivatives have not been described previously. The monochloro compounds

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