

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 methylfluorenecarboxylic acid, $C_{15}H_{10}O_3$: C, 75.6; H, 4.2. Calcd. for dimethylfluorenecarboxylic 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 methylfluorenecarboxylic acid, $C_{15}H_{10}O_3$: C, 80.4; H, 5.3; N, 6.7. Found: C, 79.9; H, 5.7; N, 6.3.

BUREAU OF MINES, REGION VIII
FUELS-TECHNOLOGY DIVISION
SYNTHETIC FUELS RESEARCH BRANCH
BRUCETON, PENNA.

RECEIVED OCTOBER 8, 1951

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 alcohols¹ 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 review² Brusson 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-dimethyl lactamide 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.

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

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

Sodium or potassium (dissolved in the lactate) was the only effective catalyst found. Neither solid nor concentrated aqueous potassium hydroxide nor Triton B, Brusson'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_D^{20} 1.4523; d_4^{20} 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_D^{20} 1.4333; d_4^{20} 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_D^{20} 1.4302; d_4^{20} 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_D^{20} 1.4344; d_4^{20} 1.0680; *MR*, calcd., 37.56; found, 38.36; and sapn. equiv., calcd., 157; found, 166.

Acknowledgment.—The authors are indebted to C. O. Willits, C. L. Ogg and their associates for the analytical data shown.

EASTERN REGIONAL RESEARCH LABORATORY³

PHILADELPHIA, PENNA.

RECEIVED OCTOBER 12, 1951

(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 JOSEPH¹

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

(1) This work was supported by a grant from the Research Corporation.

have been mentioned² but have not been described. The data for the derivatives are given in Table I. The method used in the preparation of these compounds is essentially that of Walther and v. Pulawski.³

TABLE I

| o-Phenylene- diamine condensed with, acid | Yield, % | M. p., °C. | Formula | Analyses, % | | | |
|--|-------------|------------------|--|-------------|-------|--------|-------|
| | | | | Nitrogen | | Halide | |
| | | | | Calcd. | Found | Calcd. | Found |
| o-Chlorobenzoic | 41 | 234 | C ₁₁ H ₇ N ₂ Cl | 12.25 | 12.32 | 15.5 | 14.9 |
| m-Chlorobenzoic | 44 | 238 | | | 12.20 | | 14.8 |
| p-Chlorobenzoic | 49 | 303 | | | 12.58 | | 15.0 |
| o-Bromobenzoic | 22 | 246 | C ₁₁ H ₇ N ₂ Br | 10.26 | 10.52 | 29.3 | 28.7 |
| m-Bromobenzoic | 35 | 252 | | | 10.30 | | 29.4 |
| p-Bromobenzoic | 31 | 299 | | | 10.24 | | 29.5 |
| o-Iodobenzoic | 26 | 258 | C ₁₁ H ₇ N ₂ I | 8.75 | 8.97 | 39.7 | 40.1 |
| m-Iodobenzoic | 23 | 262 | | | 8.86 | | 39.4 |
| p-Iodobenzoic | 22 | 308 | | | 8.82 | | 39.4 |

* All melting points were determined by means of a Fischer-Johns hot-stage melting point block.

Experimental

o-Phenylenediamine (0.1 mole) and the appropriate halo-benzoic acid (0.11 mole) were heated in a tall beaker covered by a watch glass to about 180° (210° for the *p*-haloacids) in an oil-bath. The mixture was stirred occasionally and sublimed crystals of the acid were returned to the reaction mixture by means of a stirring-rod. After 45 minutes of heating the mass was allowed to cool then ground in a mortar with saturated sodium carbonate solution to remove excess acid. After filtration the residue was repeatedly crystallized (charcoal) from aqueous alcohol. All the pure compounds were white crystalline substances.

(2) C. Wiegand and E. Merkel, *Ann.*, **557**, 242 (1947).

(3) R. Walther and v. Pulawski, *J. prakt. Chem.*, [2] **59**, 249 (1899).

SAN DIEGO STATE COLLEGE
SAN DIEGO, CALIFORNIA

RECEIVED AUGUST 13, 1951

Hydrogenation of Esters of L-Alanine and L-Leucine over Copper-Chromium Oxide Catalyst

BY EDWARD SEGEL

The hydrogenation of optically active α -amino esters at 175° using copper-chromium oxide catalyst has been reported to yield a racemized product.¹ It was concluded that a lower operating temperature is necessary to retain optical configuration and Raney nickel was turned to as being an effective catalyst at lower temperatures.^{2,3,4}

The fundamental assumption of these researches, that copper-chromium oxide catalyst is not suitable for the hydrogenation of optically active amino esters, is unjustified. The results described in this paper demonstrate that copper-chromium oxide is in fact the catalyst of choice, giving excellent yields of optically active amino alcohols, without the necessity of using large amounts of catalyst.

The two esters hydrogenated, L-alanine butyl ester and L-leucine ethyl ester, were prepared from the commercial amino acids. The specific rotations of the amino alcohols prepared from these two esters, +18.2° and +3.8°, compare favorably with the values of +20.1° and +4.2° previously

(1) C. C. Christman and P. A. Levene, *J. Biol. Chem.*, **124**, 453 (1938).

(2) G. Ovakimian, C. C. Christman, M. Kuna and P. A. Levene, *ibid.*, **134**, 151 (1940).

(3) H. Adkins and A. A. Pavlic, *THIS JOURNAL*, **69**, 3039 (1947).

(4) H. Adkins and H. R. Billica, *ibid.*, **70**, 3121 (1948).

obtained⁵ by reduction of the amino esters with lithium aluminum hydride.

Experimental

Dioxane used as reaction medium was purified according to the method of Fieser.⁶ L-Leucine ethyl ester was synthesized from L-leucine (from the Nutritional Biochemicals Corporation), by refluxing a solution containing 1-mole proportion of the amino acid, 10-mole proportions of absolute ethanol, and 1.5-mole proportions of sulfuric acid for 24 hours. The solvent was stripped off *in vacuo*, the residue brought to pH 10, and the free ester extracted with benzene. The extract was distilled through a 6" Vigreux column, and L-leucine ethyl ester collected from 64.0–64.5° (4.0 mm.); rotation $[\alpha]^{25}_D$ +9.6° (pure liquid); $[\alpha]^{25}_D$ +20.8° (*c* 2, methanol).

L-Alanine butyl ester was prepared by the esterification of L-alanine (from the Bios Laboratories). Boiling point of the product after fractionation was 72–73° (10 mm.); neutral equivalent: found, 146; theory, 145.

Hydrogenations were effected in a 480-ml. stainless steel bomb fitted with a thermocouple well in the base. The bomb was rocked through a 45° arc 36 times per minute. It was charged with 0.2 mole of ester, 170 ml. of dioxane and 30% as much copper-chromium oxide catalyst as ester; the contents were then equilibrated to approximately 2000 p.s.i. hydrogen pressure. The vessel was heated, and maintained at temperature until the pressure remained constant for one hour. The bomb was quenched with cold water. After centrifuging out the catalyst, the reaction mixture was distilled *in vacuo*.

Hydrogenation of L-Leucine Ethyl Ester.—L-Leucine ethyl ester was hydrogenated for 3 hours at 150°. The reaction mixture was distilled from a Claisen flask *in vacuo*, air being bubbled in through a tube containing Ascarite absorbent. Product was collected from 74–77° (1.4 mm.); yield, 85%, neutral equivalent, 120 (theory for L-leucinol, 117); rotation $[\alpha]^{25}_D$ +3.3° (*c* 3.5, methanol).

L-Leucinol was redistilled through a 6" Vigreux column; the middle cut boiled from 73–74° (1.4 mm.); neutral equivalent, 119; rotation $[\alpha]^{25}_D$ +3.8° (*c* 3.5, methanol).

Anal. Calcd. for C₉H₁₅NO: C, 61.5; H, 12.9; N, 11.9. Found: C, 61.0; H, 13.2; N, 12.4.

Hydrogenation of L-Alanine Butyl Ester.—This compound was hydrogenated under the same conditions as was L-leucine ethyl ester. Reaction temperature was maintained for 4.5 hours. L-Alaninol distilled from 56–60° (0.5 mm.), yield 55%; neutral equivalent, 77, theory, 75. Redistillation through a 3" Vigreux column gave a product boiling from 50–52° (1.5 mm.), neutral equivalent 76; rotation $[\alpha]^{25}_D$ +18.2° (*c* 2, methanol).

Anal. Calcd. for C₈H₉NO: N, 11.5. Found: N, 11.1.

(5) P. Karrer, P. Portmann and M. Suter, *Helv. Chim. Acta*, **31**, 1817 (1948).

(6) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 369.

GEORGE M. MOFFETT RESEARCH LABORATORIES

CORN PRODUCTS REFINING COMPANY

ARGO, ILLINOIS

RECEIVED JULY 13, 1951

Some Syntheses of Compounds Related to Julolidine¹

BY PETER A. S. SMITH AND TUNG-YIN YU

Incidental to a study of 9-substituted julolidines,² some attempts were made to find alternative general synthetic procedures for the julolidine ring system. Our limited success in this direction is reported here.

The successful cyclization of anilides of β -chloropropionic acid by fusion with aluminum chloride

(1) From part of the doctoral dissertation of Tung-yin Yu, 1951.

(2) Forthcoming communication; cf. Abstracts of Papers of the Chemistry Section, Meeting of The Australian and New Zealand Association for the Advancement of Science, Brisbane, Qld., May, 1951.