phosphate, b.p. 131–133° (1 mm.); was insoluble in water, soluble in toluene and ether; did not decolorize bromine in carbon tetrachloride at room temperature; $\eta^{20}\text{D}$ 1.4866.

Anal. Calcd. for $C_9H_{12}O_4Cl_3P$: Cl, 33.08; P, 9.63. Found: Cl, 32.5; P, 9.43.

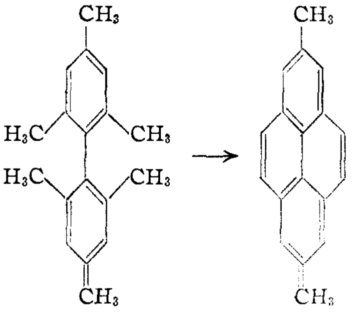
SOUTHERN REGIONAL RESEARCH LABORATORY
NEW ORLEANS, LOUISIANA
RECEIVED NOVEMBER 2, 1951

Aromatic Cyclodehydrogenation. XI. Experiments with Dimesityl[1]

BY MILTON ORCHIN, LESLIE REGGEL AND R. A. FRIEDEL

In a continuation of cyclodehydrogenation experiments[2] designed to demonstrate conversion of simple aromatics to polynuclear compounds at temperatures comparable to those employed in the pyrolysis of coal, the behavior of dimesityl was studied. It has been shown previously that vapor-phase treatment of di-*o*-tolyl leads to 4-methylfluorene,[3] but with dimesityl it might be expected that the cyclization would be forced to give phenanthrenes and pyrenes. If demethylation occurred before cyclodehydrogenation, substituted fluorenes would be obtained.

A series of cyclodehydrogenation experiments under various conditions using sulfur, palladium-on-charcoal, selenium and chromia-on-alumina catalysts is described below. In only one case was a compound isolated to which a structure could unequivocally be assigned; treatment of 17.8 g. of dimesityl over chromia-on-alumina at 500° gave 3 mg. of 4,9-dimethylpyrene



In other experiments, evidence of less highly substituted pyrenes and mixtures of phenanthrenes and fluorenes was also obtained.

Experimental

The many ultraviolet spectra employed as a means of identifying the ring systems of various fractions were determined with a Beckman spectrophotometer and with a Cary Recording Spectrophotometer, using 95% ethanol as solvent. Because pure compounds were seldom isolated and the spectra of all the parent polynuclear ring systems are well-known and are collated elsewhere,[4] no spectra are given in this paper. We wish to thank Lois Pierce, Ruth Borgman, Lois Harnack, Marian Springer and Robert Zange for the spectra determinations. Microanalyses are by G. L. Stragand, University of Pittsburgh.

Sulfur Dehydrogenation (**a**).—Dimesityl was heated with sulfur for 0.5 hour at 270–280°. No fluorescent products were obtained.

(b).—A mixture of 14.09 g. of dimesityl and 15.20 g. of sulfur was heated at 320–360° for 15 minutes. Gas was evolved rapidly, and the material became black and tarry and foamed vigorously, but showed no tendency to distil. On cooling, a black, brittle, feathery mass formed. This was extracted with benzene (soxhlet, 24 hours). An attempt to remove the sulfur by chromatography failed. The solvents were distilled off, the product was dissolved in alcoholic potassium hydroxide, and the sulfur was oxidized to sulfate by means of hydrogen peroxide.[5] There was obtained 1.15 g. of red, tarry material, not further investigated.

In a preliminary experiment, a mixture of anthracene, pyrene and sulfur was treated with hydrogen peroxide in the presence of alcoholic alkali. Precipitation of the sulfur as barium sulfate resulted in a quantitative recovery; the organic fraction was colorless and gave no test for an anthraquinone, showing that no oxidation of the hydrocarbons had occurred.

(**c**).—A mixture of 5.00 g. of dimesityl and 2.69 g. of sulfur was heated at 245–255° (bath) for 15 minutes; there was no apparent reaction. The mixture was then distilled at the water-pump (bath temperature 275–290°); some gas was evolved. The residue was a tar. The distillate (2.50 g.) was chromatographed; no fluorescent band was found. Impure dimesityl (1.87 g.) was obtained; the absence of pyrenes and phenanthrenes was confirmed by the ultraviolet spectrum.

Selenium Dehydrogenation.—Dimesityl was heated with selenium in a sealed tube (a) for 27 hours at 344–420°; (b) for 8 days at 260–400°. In both experiments the products were chromatographed to give small amounts of fluorescent oils, but no crystalline material was obtained.

Palladium-on-charcoal Dehydrogenation (**a**).—Dimesityl heated up to 350° with palladium-on-charcoal[2,6] did not evolve gas.

(b).—During 3 hours, 1.89 g. of dimesityl was passed through a furnace[2] packed with palladium-on-charcoal[2,6] at 495–510°. The product (1.22 g.) was chromatographed on alumina–supercel. The fluorescent band gave 0.24 g. of an oil which was treated with *s*-trinitrobenzene. The complex (90 mg., m.p. 137–185°) was recrystallized twice from methanol, giving 3 mg. of material, m.p. 207–240°. The ultraviolet spectrum was that of pyrene, not of an alkyl pyrene.

Chromia-on-alumina Dehydrogenation (**a**).—During 3 hours, 17.80 g. of dimesityl was passed over 81 g. of chromia-on-alumina[7] catalyst at 475–525°. The product (16.94 g.) was recrystallized from 95% alcohol, giving 13.82 g. of unreacted dimesityl. The mother liquor was freed of alcohol, taken up in petroleum ether, chromatographed on alumina, and the blue fluorescent band eluted with benzene. The fluorescent material (1.18 g.) was then rechromatographed on alumina–supercel, and a purple-fluorescent band (0.79 g. of crystalline material) was separated. Fractional crystallization from ethanol and methanol gave, as the least soluble fraction, 3 mg. of material that began to soften at 216° and had a melting point of 228.0–232.0. This was identified as 4,9-dimethylpyrene by conversion to the 2,4,7-trinitrofluorenone complex, m.p. 227.3–228.0°, not depressed by an authentic sample.[8] The balance of the material was intensively investigated by means of chromatography and complexes with picric acid and *s*-trinitrobenzene, but no pure material could be isolated. Ultraviolet absorption spectra indicated the presence of pyrene derivatives other than 4,9-dimethylpyrene and of derivatives of phenanthrene, fluorene and 9,10-dihydrophenanthrene.

(b).—Sixteen grams of dimesityl was contacted with 2.09 g. of Cr-181 catalyst[7] at 414–450° and 127–150 p.s.i. (nitrogen atmosphere) for $5^3/_4$ hours in a small pressure-extraction apparatus. The black, tarry product was dissolved in benzene, chromatographed on alumina, and the column eluted. The fractions were taken to dryness and the ultraviolet spectra were determined. There was obtained 7.82 g. of dimesityl, 0.05 g. of a colorless oil consisting of dihydrophenanthrenes and dimesityl, 0.82 g. of a pale-yellow oil consisting of substituted dihydrophenanthrenes and fluorenes, 0.49 g. of a pale-yellow oil consisting of fluorenes and phenanthrenes, 0.13 g. of white low-melting solid consisting

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(1) Not subject to copyright.

(2) M. Orchin, L. Reggel, R. A. Friedel and E. O. Woolfolk, Bureau of Mines Technical Paper 708 (1948).

(3) M. Orchin, THIS JOURNAL, **67**, 122 (1945).

(4) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(5) *U. S. Pharmacopeia*, **12**, 446 (1942).

(6) R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940); catalyst-d.

(7) Harshaw Chemical Co., Cleveland, Ohio; catalyst Cr-181.

(8) E. O. Woolfolk, M. Orchin and H. H. Storch, *Fuel*, **26**, 78 (1947).

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.

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 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.

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

EASTERN REGIONAL RESEARCH LABORATORY[3]
PHILADELPHIA, PENNA.
RECEIVED OCTOBER 12, 1951

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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.

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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[1] This work was supported by a grant from the Research Corporation.