of either component adsorbed is a linear function of its partial pressure, independent of the presence or absence of the other component, the two best lines showing this relationship were calculated by the method of least squares. In the equation $p = aV$ in which p is the partial pressure and V is the volume adsorbed, the constant a is 7.35 for oxygen and 7.26 for argon. (Pressure has been taken as the dependent variable for consistency with the graphs of Lambert and Heaven.) The pressures calculated from these equations are included in the table. In evaluating the data, it should be considered that the rated accuracy of the oxygen analyzer is ± 1% of full scale, or ± 2.3 mm.

As an additional characterization of the sample used, an adsorption–desorption isotherm for oxygen on 0.82 g. at −194.6° is shown in Fig. 1.

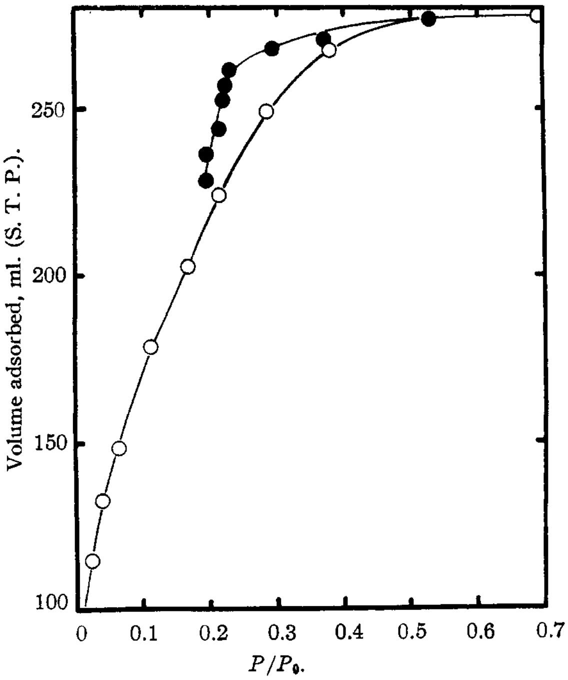

Fig. 1.—Adsorption–desorption isotherm for oxygen at −194.6°: ○, adsorption; ●, desorption.

With forced circulation of oxygen–argon mixtures through the sample used here, it is certainly not true that "the composition of the adsorbed phase is greatly affected by the order in which the two gases reach the gel surface." Unless there are vital differences between the sample used here and that of Lambert and Heaven it must be concluded that their results represented a pseudo-equilibrium, attributable to the slowness of diffusion.

The "washing out" procedure which Lambert and Heaven found to be prerequisite to reproducibility had no effect here. This is shown by the reproducibility and reversibility obtained in most of the runs without "washing out," and by the complete absence of any change in run no. 11, when it was used.

SOUTHERN RESEARCH INSTITUTE
BIRMINGHAM, ALABAMA RECEIVED JANUARY 24, 1949

The Reduction of Phenanthridine by Lithium Aluminum Hydride

BY W. C. WOOTEN[1] AND R. L. MCKEE

Lithium aluminum hydride has been found to convert phenanthridine into 5,6-dihydrophenanthridine in boiling ether in a molar ratio of 1:2.5. The reduction did not proceed beyond the dihydro stage with a larger excess of hydride (molar ratio of 1:1) under the conditions employed. Addition of the hydride to phenanthridine in boiling ether likewise gave a comparable yield of 5,6-dihydrophenanthridine.

Experimental

Forty grams (0.22 mole) of phenanthridine was introduced by use of a Soxhlet extractor into a well-stirred solution of 3.2 g. (0.087 mole) of lithium aluminum hydride in 500 cc. of anhydrous ether over a period of ten hours. The excess hydride was destroyed by addition of wet ether after which a solution of 70 cc. of hydrochloric acid in 500 cc. of water was added. It was necessary to filter at this stage to remove precipitated dihydrophenanthridine hydrochloride. The ether layer was discarded and the solid hydrochloride was combined with the aqueous solution and made strongly basic (sodium hydroxide). The product was extracted four times with a total of 1100 cc. of ether. The resulting solution was dried (magnesium sulfate) and the ether distilled. A single recrystallization from petroleum ether afforded 32.5 g. of material melting at 123–125°. A second crystallization yielded 30 g. (74%) of 5,6-dihydrophenanthridine. The melting point of this product was 123.5–124.5°, at variance with the value reported by Pictet and Ankersmit[2] but in agreement with recent workers.[3]

Anal. Calcd. for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 86.01; H, 6.12; N, 7.61.

Treatment of the dihydro compound in pyridine with benzoyl chloride formed the 5-benzoyl derivative, m. p. 90.5–92.5°.

Anal. Calcd. for $C_{20}H_{15}NO$: N, 4.91. Found: N, 4.97.

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[1] Tennessee Eastman Corporation Fellow.

[2] Pictet and Ankersmit, *Ann.*, **266**, 138 (1891).

[3] Diesbach and Aeschbach, *Helv. Chim. Acta*, **28**, 1392 (1945); Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **78**, 134 (1945), through *C. A.*, **40**, 876 (1946).

THE VENABLE CHEMICAL LABORATORY
THE UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C. RECEIVED FEBRUARY 12, 1949

α- and β-Bromocrotonolactones

BY M. C. WHITING

In reviewing the literature concerning the stereochemistry of mono-adducts formed by acetylenic compounds, it was noticed that Lespieau and Viguier[1] obtained by the action of hydrobromic acid on γ-hydroxytetrolic acid a bromocrotonolactone, m. p. 77°, which had been

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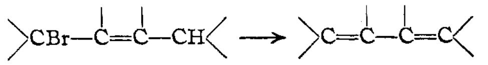
[1] Lespieau and Viguier, *Compt. rend.*, **146**, 295 (1908); *Ann. chim.*, **27**, 178 (1912).

previously obtained by Hill and Cornelison[2] and formulated by them as the α-isomer. This reaction would have been expected to give the β-isomer, which had also been prepared by Hill and Cornelison and was reported by them[2] to have m. p. 58°. These authors, however, had assigned these structures to the two isomers because the lactone, m. p. 58°, was obtained by acid hydrolysis of a substance regarded as "3,5-dibromo-2-furoic acid"[3] and it was shown by Gilman, Vander Wal, Franz and Brown[4] that this substance is actually 4,5-dibromo-2-furoic acid. The confusion originated in Hill and Sanger's erroneous assumption that the action of alkali on 2-furoic acid tetrabromide could give only the two vicinal-dehydrobromination products, the 3,4- and the 3,5-dibromo-acids. If the possibility of dehydrobromination of the type



is admitted, the formation of the 4,5-dibromo-2-furoic acid can be understood.

In view of the work of Gilman, *et al.*,[4] the formulations of the lactones must be interchanged (*i. e.*, α-bromocrotonolactone has m. p. 58° and β-bromocrotonolactone, m. p. 77°). The addition of hydrogen bromide to γ-hydroxypropiolic acid therefore follows the usual rule, and the "α-anilinocrotonolactone," m. p. 217–218°, obtained by Hill and Cornelison[2] by treating the supposed α-bromocrotonolactone with aniline, is presumably the β-isomer, *i. e.*, tetronic acid anilide, for which Wolff[5] gives m. p. 220°.

[2] Hill and Cornelison, *Am. Chem. J.*, **16**, 277 (1894).

[3] Hill and Sanger, *Proc. Am. Acad. Arts Sci.*, **21**, 135 (1885).

[4] Gilman, Vander Wal, Franz and Brown, THIS JOURNAL, **57**, 1146 (1935).

[5] Wolff, *Ann.*, **315**, 156 (1901).

THE UNIVERSITY
MANCHESTER, ENGLAND

RECEIVED MARCH 10, 1949

Complexes of Urea with Linear Aliphatic Compounds

BY W. J. ZIMMERSCHIED, R. A. DINERSTEIN, A. W. WEITKAMP AND ROBERT F. MARSCHNER

We have confirmed and extended the observation made nearly a decade ago by Bengen[1] that urea has the property of forming complexes with straight-chain organic compounds, but not with their branched and cyclic analogs. No later reference to this interesting property of urea appears in the chemical literature despite its utility, which is illustrated by the following example:

To 0.100 mole of n-hexadecane (n^{20}D 1.4345) diluted with 9 volumes of mixed decahydronaphthalenes (n^{20}D 1.4766) were added 1.5 moles of urea and 0.15 mole of methanol, and the suspension was stirred at 25° for forty-five minutes. The mass was filtered by suction, washed on the filter three times with 500 ml. of isopentane and decomposed in 300 ml. of water. The liberated hydrocarbon was taken up in 100 ml. of ether, and the separated ether layer was evaporated (with residual isopentane) to leave 0.097 mole of n-hexadecane, n^{20}D 1.4343.

The formation of urea-n-hexadecane is accompanied by the evolution of 23 kcal. per mole of n-hexadecane and the complex contains 11 moles of urea. Halogen, sulfur and various oxygen derivatives form entirely similar complexes if the linearity of the carbon skeleton is preserved. Compounds with a single methyl branch form complexes when the linear chain approaches 20, the exact number depending upon the nature of the substituent and the position of the methyl group.

[1] Friederich Bengen, German patent application O. Z. 12438 (March 18, 1940); Technical Oil Mission Reel 6, frames 263–270 (in German), and Reel 143, pages 135–139 (in English).

RESEARCH DEPARTMENT
STANDARD OIL CO. (INDIANA)
WHITING, INDIANA

RECEIVED MAY 16, 1949

NEW COMPOUNDS

Alkyl Ethers of 2-Nitro-1-butanol[1]

In the course of a current investigation the methyl, ethyl and propyl ethers of 2-nitro-1-butanol were required. These ethers have apparently not heretofore been reported in the literature. They were prepared by the method recently described by Lambert,[2] which involves the addition of the appropriate sodium alcoholate to the nitro-olefin. The required 2-nitro-1-butene was prepared by the method of Blomquist and Shelley.[3] Using a small quantity of the nitrobutene, 16 to 50 g., the yield of purified ether was between 40 and 50%. Certain physical constants and the nitrogen analyses[4] of the three nitro ethers follow:

Ether	B. p. at 10 mm., °C.	n^{20}D	d^{25}_4	Molecular refractivity Calcd.	Found	Nitrogen, % Calcd.	Found
Me	75.0–75.5	1.4217	1.0233	33.00	32.56	10.52	10.48
Et	83.0–83.2	1.4210	0.9975	37.15	37.46	9.57	9.56
Pr	94.5–95.0	1.4238	0.9780	41.77	41.99	8.70	8.74

[1] This work was done on a Frederick Gardner Cottrell Grant given by the Research Corporation.

[2] A. Lambert, British Patent 584,792; through *Chem. Abstr.*, **41**, 5144 (1947).

[3] A. T. Blomquist and T. H. Shelley, THIS JOURNAL, **70**, 147 (1948).

[4] Nitrogen analyses were made by Mr. H. Galbraith of the Purdue Department of Chemistry using the micro Dumas method.

DEPARTMENT OF CHEMISTRY AND
PURDUE RESEARCH FOUNDATION
PURDUE UNIVERSITY WILLIAM J. SEAGERS
LAFAYETTE, INDIANA PHILIP J. ELVING

RECEIVED APRIL 23, 1949

The Preparation and Characteristics of the 2,4-Dinitrophenylhydrazones of Several Androgens[1]

In connection with the development of a procedure for the separation of the estrogens from the androgens the following steroid hormone 2,4-dinitrophenylhydrazones were prepared according to the method of Hilmer and Hess[2] and their absorption maxima were determined.

[1] This investigation was supported by a grant from the United States Public Health Service.

[2] Hilmer and Hess, *Anal. Chem.*, in press.