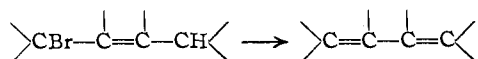


previously obtained by Hill and Cornelison<sup>2</sup> and formulated by them as the  $\alpha$ -isomer. This reaction would have been expected to give the  $\beta$ -isomer, which had also been prepared by Hill and Cornelison and was reported by them<sup>2</sup> to have m. p. 58°. These authors, however, 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"<sup>3</sup> and it was shown by Gilman, Vander Wal, Franz and Brown<sup>4</sup> 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.*,<sup>4</sup> the formulations of the lactones must be interchanged (*i. e.*,  $\alpha$ -bromocrotonolactone has m. p. 58° and  $\beta$ -bromocrotonolactone, m. p. 77°). The addition of hydrogen bromide to  $\gamma$ -hydroxypropionic acid therefore follows the usual rule, and the " $\alpha$ -anilincrotonolactone," m. p. 217–218°, obtained by Hill and Cornelison<sup>2</sup> by treating the supposed  $\alpha$ -bromocrotonolactone with aniline, is presumably the  $\beta$ -isomer, *i. e.*, tetrionic acid anilide, for which Wolff<sup>5</sup> 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<sup>1</sup> 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

(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).

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.

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

RECEIVED MAY 16, 1949

## NEW COMPOUNDS

### Alkyl Ethers of 2-Nitro-1-butanol<sup>1</sup>

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,<sup>2</sup> which involves the addition of the appropriate sodium alcoholate to the nitroolefin. The required 2-nitro-1-butene was prepared by the method of Blomquist and Shelley.<sup>3</sup> 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<sup>4</sup> of the three nitro ethers follow:

Ether	B. p. at 10 mm., °C.	$n^{20}_D$	$d^{25}_4$	Molecular refractivity		Nitrogen, %	
				Calcd.	Found	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  
LAFAYETTE, INDIANA

WILLIAM J. SEAGERS  
PHILIP J. ELVING

RECEIVED APRIL 23, 1949

### The Preparation and Characteristics of the 2,4-Dinitrophenylhydrazones of Several Androgens<sup>1</sup>

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<sup>2</sup> 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.