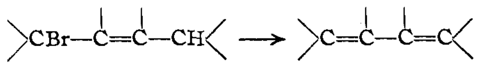
previously obtained by Hill and Cornelison[2] and formulated by them as the α-isomer. This reaction would have been expected to give the β-isomer, which had also been prepared by Hill and Cornelison and was reported by them[2] to have m. p. 58°. These authors, however, had assigned these structures to 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
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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 ($n^{20}\text{D}$ 1.4345) diluted with 9 volumes of mixed decahydronaphthalenes ($n^{20}\text{D}$ 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, $n^{20}\text{D}$ 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.

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(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 nitroolefin. 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.	$n^{20}\text{D}$	$d^{25}{}_4$	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

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(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.

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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.

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

(2) Hilmer and Hess, *Anal. Chem.*, in press.

2,4-Dinitrophenylhydrazone	M. p.,[5] °C.	Color	Nitrogen, % Found	Nitrogen, % Calcd.	Max.,[6] (chlf.), mμ	Log E_m (chlf.)	Max. (alk.), mμ
Isoandrosterone	215–216	Orange-yellow	11.17	11.27	372	5.04	400
Etiocholan-3β-ol-17-one	178–180	Yellow	11.41	11.27	370	5.05	400
Dehydroepiandrosterone[3]	237–238	Yellow-orange	12.10	12.38	370	5.02	395
17-Methyltestosterone[3]	218–221	Red-orange	12.24	12.00	395	5.25	430
Equilenin[4]	268–270	Orange-yellow	13.44	13.01	370	5.01	350, 390

Acknowledgment.—The authors are indebted to Dr. Arthur St. André of Ciba Pharmaceutical Products, Inc., who supplied the hormones used in this investigation.

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[3] Johnston, *Science*, **106**, 91 (1947).

[4] Veitch and Milone, *J. Biol. Chem.*, **157**, 417 (1945).

[5] The melting points were determined on a Fisher–Johns apparatus.

[6] Spectroscopic Analysis.—Solutions of the five DNPH derivatives in chloroform (1 ml. equivalent to 25 micrograms of free hormone) were subjected to analysis in the Beckman quartz spectrophotometer in the region 255 mμ to 500 mμ. The effect of alkali on the spectra was determined by treatment of the steroid DNPH derivatives (1 ml. of chloroform solution equivalent to 75 micrograms of free hormone) with 0.1 *N* alcoholic potassium hydroxide, and measurement of per cent. transmittance in a Coleman spectrophotometer in the region 350 to 600 mμ. The maxima were shifted toward the visible region of the spectrum in each case, with the exception of equilenin DNPH, which exhibited two maxima, one toward the ultraviolet, the other toward the visible. A similar discrepancy in the shifting of spectra with alkali has been noted by Roberts and Green.[7]

[7] Roberts and Green, THIS JOURNAL, **68**, 214 (1946).

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Some Acetylenic Compounds[1]

Propargyl Formate.—A mixture of 56 g. of propargyl alcohol and 46 g. of anhydrous formic acid was heated to boiling, and 30 g. of powdered calcium chloride was added. After standing overnight in a stoppered flask, the liquid was decanted and distilled through a 40-cm. Vigreux column. A main fraction was taken from 95–110° and a second fraction from 110–118°. The second fraction was reesterified with 12 g. of formic acid and 8 g. of calcium chloride. Most of the product distilled below 110°. The fractions boiling at 95–110° were combined, cooled in ice, two volumes of ether added and the solution washed with cold aqueous sodium bicarbonate. After drying over calcium chloride and fractionating through a 40-cm. Vigreux column, 28 g. (35%) distilled at 105–109°; $n^{18.5}\text{D}$ 1.4203.

Anal.[2] Calcd. for $C_4H_4O_2$: C, 57.14; H, 4.80. Found: C, 56.75, 56.74; H, 5.44, 5.45.

Methyl Bromopropiolate.—To a solution of 75 g. of bromopropiolic acid in 600 cc. of methanol was added slowly 185 g. of concentrated sulfuric acid with shaking and cooling under tap water. After standing six days the solution was poured onto 1.5 kg. of ice and extracted with five 200-cc. portions of ether. The extracts were dried over anhydrous magnesium sulfate and the ether and alcohol removed under reduced pressure. The product was distilled twice at 5 mm. pressure from a Claisen flask having a 20-cm. fractionating side arm to give 62 g. (75%), b. p. 40–45° at 5 mm., $n^{25}\text{D}$ 1.4884.

Anal. Calcd. for $C_4H_3O_2Br$: C, 29.47; H, 1.85. Found: C, 29.50, 29.52; H, 1.99, 2.01.

The product is unstable and soon turns dark red. After standing a month, about one-third had polymerized.

2-Chloroethyl Propiolate.—This ester was prepared from 43 g. of propiolic acid, 175 g. of anhydrous ethylene chlorohydrin and 18 g. of concentrated sulfuric acid by the procedure given for methyl bromopropiolate. The yield after two fractionations was 43 g. (53%), b. p. 79–82° at 17 mm.; $n^{20}\text{D}$ 1.4588.

Anal. Calcd. for $C_5H_5O_2Cl$: C, 45.30; H, 3.80. Found: C, 45.30, 45.17; H, 3.90, 3.86.

Allyl Propiolate.—A mixture of 100 g. of propiolic acid, 500 g. of allyl alcohol, and 45 g. of concentrated sulfuric acid was allowed to stand for two days and the ester isolated as above. The yield was 46 g. (30%), b. p. 70–73° at 60 mm.; $n^{18.5}\text{D}$ 1.4378.

Anal. Calcd. for $C_6H_6O_2$: C, 65.44; H, 5.49. Found: 65.42, 65.49; H, 5.72, 5.67.

Isopropyl Acetylenedicarboxylate.—A mixture of 50 g. of acetylenedicarboxylic acid, 200 g. of dry isopropyl alcohol, 5 g. of *p*-toluenesulfonic acid and 0.2 g. of hydroquinone was placed in a 500-cc. flask fitted with a 40-cm. Vigreux column and a condenser set for distillation. The mixture was heated on an oil-bath, the temperature of which was raised slowly from 110 to 135° until 145 g. of isopropyl alcohol had distilled at 80–81° during two hours. The mixture was cooled, poured into 400 cc. of water, extracted with three 100-cc. portions of ether, washed with sodium bicarbonate solution, and dried over calcium chloride. The ether was evaporated, 0.2 g. of hydroquinone added, and the product distilled at reduced pressure from a modified Claisen flask. The yield was 39 g. (45%), b. p. 103–107° at 4 mm.; $n^{18.5}\text{D}$ 1.4408.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.09, 60.20; H, 7.23, 7.27.

Allyl Acetylenedicarboxylate.—This ester was prepared from 50 g. of acetylenedicarboxylic acid, 200 g. of allyl alcohol, 3 g. of *p*-toluenesulfonic acid, and 0.2 g. of hydroquinone by a procedure analogous to that for isopropyl acetylenedicarboxylate. The yield was 61 g. (70%) b. p. 112–118° at 4 mm., $n^{18.5}\text{D}$ 1.4718.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.84; H, 5.19. Found: C, 61.62, 61.68; H, 5.39, 5.30.

Methoxytetrolic Acid.—In a 2-liter three-necked flask equipped with a gas inlet reaching to the bottom of the flask, a mercury-sealed stirrer, and a reflux condenser cooled with ice water, was placed 30 g. of magnesium turnings and 300 cc. of absolute ether. Methyl chloride was added from a cylinder until all of the magnesium had reacted. The gas inlet was replaced by a dropping funnel, and 75 g. of methyl propargyl ether was added. The mixture was refluxed for six hours. After cooling in an ice-bath and adding 300 cc. of dry benzene, the dropping funnel was replaced by the gas inlet and carbon dioxide passed through the mixture for four hours at 0° and four hours at 20°. The mixture was cooled to 0° and 500 cc. of cold 10% sulfuric acid was added, keeping the temperature below 5° during the addition. After reaching room temperature the ether layer was separated, and the aqueous layer was extracted with three 100-cc. portions of ether. The ether solutions were combined and extracted with aqueous sodium carbonate. The carbonate extract was acidified with 20% sulfuric acid and extracted with four 50-cc. portions of ether. The ether was evaporated, and the residue distilled at reduced pressure from a modified Claisen flask. The yield was 60 g. (49%), b. p. 114–118° at 3 mm.; $n^{20}\text{D}$ 1.4669.

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[1] These compounds were prepared for the Office of Scientific Research and Development under Contract OEMsr-136 with Stanford University.

[2] All carbon–hydrogen microanalyses by Huffman Microanalytical Laboratories, Denver, Colo.