Compounds	Formulas	M. p., °C. (uncor.)	Analyses, % N Calcd.	Found
N,N'-Methylene-di-piperidinium di-bromides				
N,N'-Di-*n*-heptyl	$C_{25}H_{52}N_2Br_2$	178	5.19	5.38
N,N'-Di-*n*-octyl	$C_{27}H_{56}N_2Br_2$	162	4.92	5.07
N,N'-Di-*n*-tetradecyl	$C_{39}H_{80}N_2Br_2$	183	3.80	3.87
N,N'-Di-*n*-hexadecyl	$C_{43}H_{88}N_2Br_2$	176	3.53	3.70
N,N'-Benzal-di-piperidinium di-bromides				
N,N'-Di-*n*-heptyl	$C_{31}H_{56}N_2Br_2$	177	4.54	4.91
N,N'-Di-*n*-octyl	$C_{33}H_{60}N_2Br_2$	165	4.34	4.45
N,N'-Di-*n*-tetradecyl	$C_{45}H_{84}N_2Br_2$	181	3.45	3.82
N,N'-Di-*n*-hexadecyl	$C_{49}H_{92}N_2Br_2$	179	3.22	3.42

THE CHEMICAL LABORATORIES OF
NEW YORK UNIVERSITY
WASHINGTON SQUARE COLLEGE
NEW YORK, N. Y., AND OF
ST. PETER'S COLLEGE JOSEPH B. NIEDERL
JERSEY CITY, N. J. ANTHONY E. LANZILOTTI

RECEIVED FEBRUARY 10, 1944

o-Biphenyl Isocyanate, *o*-Bicyclohexyl Isocyanate, N,N'-Di-*o*-biphenyl Urea, N,N'-Di-*o*-bicyclohexyl Urea

The isocyanates were prepared by the reaction of *o*-biphenylamine and *o*-bicyclohexylamine[1] with phosgene. Solutions of the amines in dry toluene were added gradually to a sixfold excess of phosgene, dissolved to 20 to 30% solution in toluene. The solutions were warmed during and after the addition of the base and finally refluxed for several hours. Most of the white crystals (hydrochloride) which formed with *o*-biphenylamine dissolved during heating. No precipitate appeared with *o*-bicyclohexylamine. Subsequently, the toluene and phosgene were distilled off; the residue was heated with carbon tetrachloride,[2] the solution was filtered if necessary, and the solvent was removed by distillation. From the residue the isocyanates were distilled as colorless oils, in yields of 60 to 70%. *o*-Biphenyl isocyanate distilled at 100° (0.5–1 mm.); *o*-bicyclohexyl isocyanate, at 89–90° (0.5–1 mm.).

o-Biphenyl isocyanate—calcd. for $C_{13}H_9NO$: N, 7.18. Found: N, 7.10.

o-Bicyclohexyl isocyanate—calcd. for $C_{13}H_{21}NO$: N, 6.75. Found: N, 6.63.

The corresponding symmetrical disubstituted ureas were prepared by treating the isocyanates with water containing 10% of pyridine as a catalyst. The biphenyl compound reacted in the cold but the bicyclohexyl isocyanate had to be heated on a steam-bath. The product obtained from the former showed a sharp and constant melting point of 182° (uncor.) after two recrystallizations from absolute alcohol. The crystals obtained from bicyclohexyl isocyanate showed a protracted melting point (218–228°) which did not become sharp after repeated recrystallizations (from methanol-water or, preferably, from dioxane). The final melting point was 225–228° (uncor.). Since several of the stereoisomeric ureas may be present, the lack of a sharp melting point is not surprising.

N,N'-Di-*o*-biphenyl urea—calcd. for $C_{25}H_{20}N_2O$: C, 82.5; H, 5.5; N, 7.7. Found: C, 82.2; H, 5.6; N, 7.2.

N,N'-Di-*o*-bicyclohexyl urea—calcd. for $C_{25}H_{44}N_2O$: C, 77.4; H, 11.4. Found: C, 77.2; H, 11.4,

We thank L. M. White for the analytical data.

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[1] The amines were kindly furnished by the Monsanto Chemical Co.

[2] Shriner, Horne and Cox, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. II, 1943, p. 453.

WESTERN REGIONAL RESEARCH LABORATORY
BUREAU OF AGRIC. AND IND. CHEM.
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE
ALBANY, CALIF. HEINZ FRAENKEL-CONRAT
HAROLD S. OLCOTT

RECEIVED FEBRUARY 14, 1944

Methyl 3-Methyl-4,6-ethylidene-α- and β-Glucosides

During the course of some work on the optical rotations of substituted glucose derivatives, preparations of the α- and β-methylglucosides of 3-methyl-4,6-ethylideneglucose were required. Catalytic deacetylation with sodium methylate of 16.5 g. of the non-crystalline triacetate, sp. rot. (D line, 25°) + 84° ($CHCl_3$, *C*, 7.8) gave 10.8 g. of a sirupy mixture of methyl 3-methyl-α- and β-glucosides. This was shaken with 45 ml. of freshly distilled paraldehyde and 0.2 ml. of concentrated sulfuric acid until solution was complete. The solution was allowed to stand at room temperature for fifteen minutes after which water and petroleum ether were added. The aqueous layer was separated, washed twice with petroleum ether, and extracted four times with chloroform. Evaporation of the chloroform solution left a crystalline mixture from which 0.6 g. of a substance of m. p. 106–107° and 0.022 g. of another of m. p. 133–134° were separated by fractional crystallization from ether–petroleum ether mixtures. An additional 0.215 g. of the high-melting substance (methyl 3-methyl-4,6-ethylidene-β-glucoside) was obtained in better yield from methyl 3-methyl-β-glucoside. Methylation of the high-melting compound with methyl iodide and silver oxide gave the known methyl 2,3-dimethyl-4,6-ethylidene-β-glucoside[1] melting at 103–105° alone or mixed with an authentic specimen, hence the high-melting compound is regarded as methyl 3-methyl-4,6-ethylidene-β-glucoside. The analyses and properties of the low-melting substance indicate that it is methyl 3-methyl-4,6-ethylidene-α-glucoside. It is noted that the difference in molecular rotation for the high and low-melting compounds is 42,120, while the corresponding value calculated for the α- and β-methylglucosides of 4,6-ethylidene glucose would be 40,920.[2]

Methyl 3-methyl-4,6-ethylidene-α-glucoside: melting point 106–107° (cor.); sp. rot. (D line, 25°) + 114° (H_2O, *C*, 0.6); (Hg blue line, 25°) + 246° (H_2O, *C*, 0.6).

Methyl 3-methyl-4,6-ethylidene-β-glucoside: melting point 133–134° (cor.); sp. rot. (D line, 25°) − 66° (H_2O, *C*, 0.7); (Hg blue line, 25°) − 126° (H_2O, *C*, 0.7).

			C	H	OCH_3
Anal.	Calcd. for $C_{10}H_{18}O_6$ (234):		51.28	7.69	26.50
	Found:	α-compound	51.5	7.79	26.3
			51.3	7.67	26.5
		β-compound	51.2	7.82	26.4
			51.1	8.07	26.5

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[1] B. Helferich and H. Appel, *Ber.*, 64, 1841 (1931).

[2] H. Appel and W. N. Haworth, *J. Chem. Soc.*, 793 (1938).

SOUTHERN REGIONAL RESEARCH LABORATORY
U. S. DEPARTMENT OF AGRICULTURE
NEW ORLEANS, LA. RICHARD E. REEVES

RECEIVED JANUARY 24, 1944

n-Nonatriacontane

During some attempts to mono-alkylate acetone dicarboxylic ester (diethyl β-ketoglutarate) with octadecyl iodide, the dialkylated ester was also formed as a by-product, which after hydrolysis and decarboxylation yielded nonatriacontanone-20. Reduction of the latter by Clemmensen's method gave *n*-nonatriacontane. An alkyl halide having *n* carbon atoms thus yields a hydrocarbon with 2*n* + 3 carbon atoms.

Nonatriacontanone-20.—To a solution of 1.15 g. of sodium in 30 cc. of dry *n*-butanol were added 10 g. of acetone-dicarboxylic ester and 19 g. of *n*-octadecyl iodide prepared from *n*-octadecanol-1 of f. p. 57.8° (thermometer in the liquid); the iodide was distilled *in vacuo* (b. p. 221–224°, 9 mm.) and crystallized twice from acetone and once from methanol–ether (2:1)) and the mixture refluxed until the reaction was neutral (ten hours). The solid which separated on cooling was collected and refluxed with 60 cc. of concentrated hydrochloric acid for 9.5 hours. The neutral material resulting from this treatment was separated and crystallized from hot ethanol; 4.5 g. of nonatriacontanone-20 melting at 90–92.5° resulted. After treatment with charcoal to remove a yellow discoloration and two recrystallizations from light petroleum (b. p. 70–80°) the ketone melted at 91.2–91.4°.[1]

The long X-ray spacing (melted specimen) was 51.5 Å., indicating that this ketone, like the lower homologs, crystallizes with vertical molecules.

Anal.[2] Calcd. for $C_{39}H_{78}O$: C, 83.1; H, 13.9. Found: C, 83.1; H, 13.9.

***n*-Nonatriacontane.**—1.9 grams of the ketone, 48 g. of amalgamated zinc, 48 cc. of concentrated hydrochloric acid and 10 cc. of glacial acetic acid were boiled under reflux. Every sixth hour the mixture was cooled, the liquid decanted and fresh hydrochloric acid, glacial acetic acid and zinc (10 g.) added. The reduction was followed by determination of the m. p. of the product. After eighty hours the m. p. became constant at 79.0–79.4°. The hydrocarbon was collected and purified by treatment with concentrated sulfuric acid at 130° for two hours.[3] Considerable darkening occurred and the process was repeated until on the fourth treatment darkening no longer took place. The hydrocarbon was carefully washed with hot water and treated with charcoal in benzene. It crystallized from benzene in small white lustrous plates and after three crystallizations from this solvent the m. p. was 80.0–80.2°. The phenomena observed on heating and cooling the hydrocarbon through the m. p. are similar to those observed for the lower homologs.[3] On heating the opaque crystalline material a transition is observed at approximately 75° (change into a transparent form with vertical rotating chains). The s. p. on cooling the melt lies at 79.8°. At this point transparent needles are formed in the melt. On further cooling to 75°, the transparent solid is changed to an opaque form stable at lower temperatures.

The X-ray investigation of the hydrocarbon, crystallized from benzene and pressed on to glass, gave a long spacing of 51.3 Å., corresponding to the normal (A) form with vertical molecules. A specimen melted on to glass by means of the hot-wire technique gave, however, a different diffraction pattern with a long spacing of 47.1 Å., indicating tilted molecules. Odd number hydrocarbons containing more than eleven carbon atoms have previously been found to crystallize only in the A form with vertical molecules.[3] The dimorphism of *n*-nonatriacontane was therefore unexpected, and the compound provides an exception to the rule[4] that a longer chain and an odd number of carbon atoms (and also a higher temperature and the presence of impurity) favors crystallization in vertical forms.

Anal.[2] Calcd. for $C_{39}H_{80}$: C, 85.4; H, 14.6. Found: C, 85.1; H, 14.6.

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[1] The m. p.'s and s. p.'s were determined in capillary tubes using a glycerol bath and totally immersed calibrated Anschütz type thermometers. Heating and cooling were carried out very slowly.

[2] Microanalysis by Dr. Max Möller, Copenhagen.

[3] S. A. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931).

[4] *Cf.* J. C. Smith, *Ann. Reports*, **35**, 259 (1938).

DEPARTMENT OF MEDICAL CHEMISTRY
UNIVERSITY OF UPPSALA
UPPSALA, SWEDEN
EINAR STENHAGEN
BIRGITTA TÄGTSTRÖM

RECEIVED MARCH 3, 1944

COMMUNICATIONS TO THE EDITOR

STERIC STRAIN AND THE ANOMALOUS BASE STRENGTH OF THE NORMAL ALIPHATIC AMINES

Sir:

The strength of the normal aliphatic acids and amines changes with chain length in a peculiar manner. Thus K_a decreases for the first three members, but increases for the fourth (Table I). This curious behavior has been ascribed in the case of the carboxylic acids to hydrogen bond formation between the end methyl group of butyric acid (or of the γ-methylene group of the higher acids) with the carbonyl oxygen of the carboxyl group.[1] A similar explanation could be used for the amines.

TABLE I

ACIDITY CONSTANTS FOR THE NORMAL ALIPHATIC ACIDS AND AMINES

R	RCOOH at 25°[a]	RNH_3^+ at 25°[b]	$RNH_2:BMe_3$ at 100°
H	17.12×10^{-5}	5.38×10^{-10}	4.62
CH_3	1.75	0.229	0.036
C_2H_5	1.33	.214	.071
n-C_3H_7	1.38	.263	.060
n-C_4H_9	1.32	.229	.047
n-C_5H_{11}	1.28	.228	.042

[a] From Dippy, ref. 1. [b] From Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932), and from Hoerr, McCorkle and Ralston, *ibid.*, **65**, 328 (1943).

As part of a study of generalized acids and bases in gaseous systems,[2] the measurement of the base strength of the normal aliphatic amines with trimethylboron as the reference acid was undertaken. The base strength thus measured (Table I) first increases markedly from ammonia to methylamine, then decreases with ethylamine, rises again with propylamine and then increases regularly. This behavior is so similar to that of the normal aliphatic acids and of the corresponding amides that it is not unreasonable to seek one fundamental explanation for the phenomena.

One important difference will be noted between the order obtained with trimethylboron and the orders obtained by classical methods. With trimethylboron the irregularity appears with the third member of the series, $C_2H_5NH_2:BMe_3$, rather than with the fourth. Since ethylamine cannot form a hydrogen bridge of the type postulated to account for the behavior of butyric acid and propylamine in aqueous solution, it is reasonable to seek some other explanation. (It might also be pointed out that according to the hydrogen bridge hypothesis the order should be independent

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[1] Dippy, *Chem. Rev.*, **25**, 151 (1939).

[2] THIS JOURNAL, **66**, 431, 435 (1944).