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

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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.

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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
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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 nonatria-