vacuo. The residue was washed with ether and crystallized from 2-propanol. The product was identical with the acid-catalyzed product **2b:** yield 60%.

3,3′-(1,1′-Octanediylidene)bis[4-hydroxy-2(5*H*)-furanone]. Following the same procedure for base catalysis, 1-octanal was reacted with tetronic acid. The white product was recrystallized at 0 °C from (1:150) ethyl acetate–cyclohexane: mp 198 °C; NMR ($CDCl_3$) δ 0.5–2.2 (m, 15 H), 3.96 (t, 1 H, J = 8 Hz), 4.72 (s, 4 H), 10.66 (s, 2 H, exchangeable with D_2O). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.71; H, 7.09

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Registry No.—**1,** 4971-56-6; (*E*)-**2a,** 65276-56-4; (*Z*)-**2a,** 65276-57-5; (*E*)-**2b,** 65276-58-6; (*Z*)-**2b,** 65276-59-7; (*E*)-**2c,** 65276-60-0; (*Z*)-**2c,** 65276-61-1; (*E*)-**2d,** 65276-62-2; (*Z*)-**2d,** 65276-48-4; (*E*)-**2e,** 65276-49-5; (*Z*)-**2e,** 65276-50-8; (*E*)-**2f,** 65276-51-9; (*Z*)-**2f,** 65276-52-0; (*E*)-**2g,** 65276-53-1; (*Z*)-**2g,** 65276-54-2; (*E*)-**2h,** 65276-55-3; (*Z*)-**2h,** 65276-37-1; (*E*)-**2i,** 65276-38-2; (*Z*)-**2i,** 65276-39-3; (*E*)-**2j,** 65276-40-6; (*Z*)-**2j,** 65276-41-7; α-bromotetronic acid, 1192-50-3; *o*-chlorobenzaldehyde, 89-98-5; *p*-chlorobenzaldehyde, 104-88-1; *o*-nitrobenzaldehyde, 552-89-6; benzaldehyde, 100-52-7; *o*-hydroxybenzaldehyde, 90-02-8; 3,4-methylenedioxybenzaldehyde, 120-57-0; cinnamaldehyde, 104-55-2; 3,4-dimethoxybenzaldehyde, 120-14-9; 4-dimethylaminobenzaldehyde, 100-10-7; 3,4,5-trimethoxybenzaldehyde, 86-81-7; triethyl phosphate, 122-52-1; 1-octanal, 124-13-0; 3,3′-(1,1′-octanediylidene)bis[4-hydroxy-2(5*H*)-furanone], 65276-34-8.

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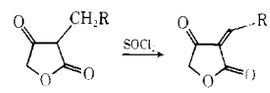
(10) Certain compounds of type **2** were recently obtained by a sequence which does not proceed via **1.** Substituted 3-benzyl-β-tetronic acids were dehydrated by thionyl chloride to give type **2** compounds. However, since the yields of this reaction were less than acceptable for a good synthetic procedure and the choice of substituents is severely limited, this pathway does not represent a generally applicable alternative pathway for the preparation of the desired furandiones **2.** See ref 6b.



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Macrocyclic Ureas as Masked Isocyanates

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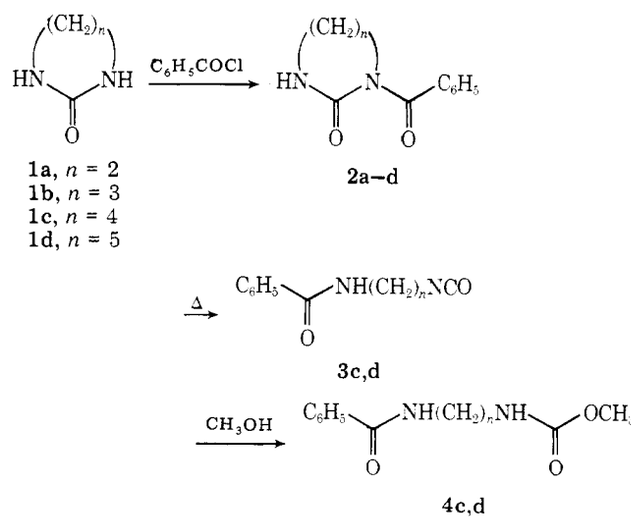
Macrocyclic *N*-aroylureas, synthesized by aroylation of macrocyclic ureas with mono- and dicarboxylic acid chlorides, undergo a facile thermal ring-opening reaction to give *N*-aroylamidoalkylene isocyanates **3.** Treatment of the crude isocyanates with methanol yields the corresponding methyl carbamates **4.**

The blocking of isocyanate groups has been attempted previously in order to formulate stable one-component polyurethane systems.[1] Heating of the blocked isocyanates generate the free isocyanates with release of the blocking agent. The ideal blocking agent should become part of the polymer backbone after release, thereby eliminating the need for well-ventilated working areas. This paper deals with the design of blocked isocyanates in which the blocking agents are incorporated into the polyurethane backbone.

The key to the design of functional blocking agents was our observation that certain 1,3-disubstituted ureas undergo facile thermal dissociation to produce isocyanate and an amine derivative.[2] If the urea group is part of a cyclic system, both fragments could conceivably be incorporated into a growing polymer chain. In order to test this hypothesis, the *N*-benzoylureas **2** were synthesized as model compounds. While the five- and six-membered ring ureas **2a** and **2b** (n = 2 and 3) did not appreciably dissociate upon heating in an inert high-boiling solvent, the seven- and eight-membered ring ureas **2c** and **2d** undergo ring opening on refluxing in *o*-dichloroben-

Scheme I



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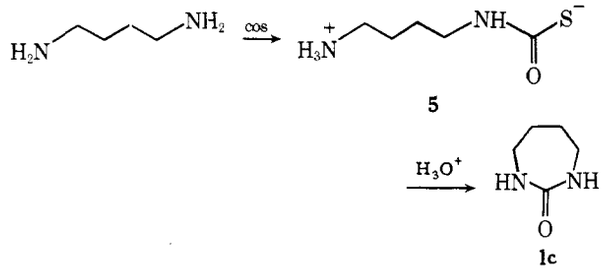
zene to give the corresponding novel benzoylamidoalkyl isocyanates **3**, as evidenced by infrared spectroscopy (NCO at 2270 cm^{-1}) and conversion into methyl ω-benzoylamidoalkyl carbamates **4c** and **4d** on heating with excess methanol (Scheme I). Heating of **1c** and **1d** with excess methanol in benzene did not yield the corresponding carbamates **4c** or **4d.**

The required seven- and eight-membered ring macrocyclic ureas were synthesized by novel procedures. Reaction of tetramethylenediamine with carbonyl sulfide gives rise to the formation of the inner salt **5**, which was treated without isolation with concentrated hydrochloric acid to give perhydro-1,3-diazepin-2-one (**1c**).

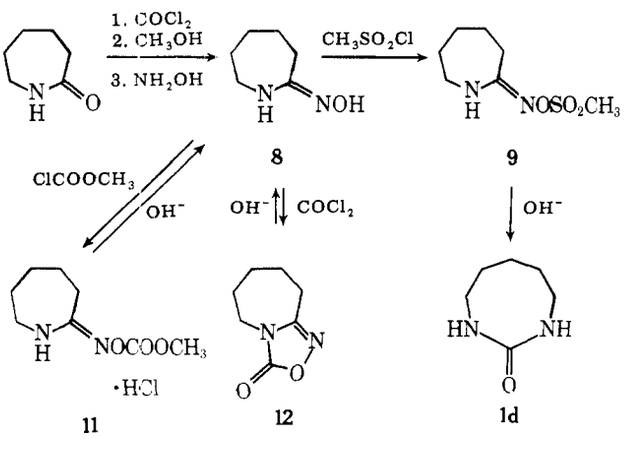


The synthesis of the eight-membered ring urea, perhydro-1,3-diazocin-2-one (**1d**), starting with caprolactam required several steps (see Scheme II) but gave satisfactory yields in all of them. Thus, low-temperature phosgenation of caprolactam produces 3,4,5,6-tetrahydro-7-chloro-2*H*-azepine[3] which on treatment with methanol gives 3,4,5,6-tetrahydro-7-methoxy-2*H*-azepine (**7**) in 65–70% yield. The lactam ether **7** converts with hydroxylamine to the amide oxime **8** which is easily converted to the mesylate **9**. Lossen rearrangement of **9** in base gives the desired cyclic urea **10** in nearly quantitative yield. The last step was found to be superior to all other known procedures for the preparation of pentamethyleneurea from **8**,[4] the tosylate of **8**,[5] or other precursors.[6]

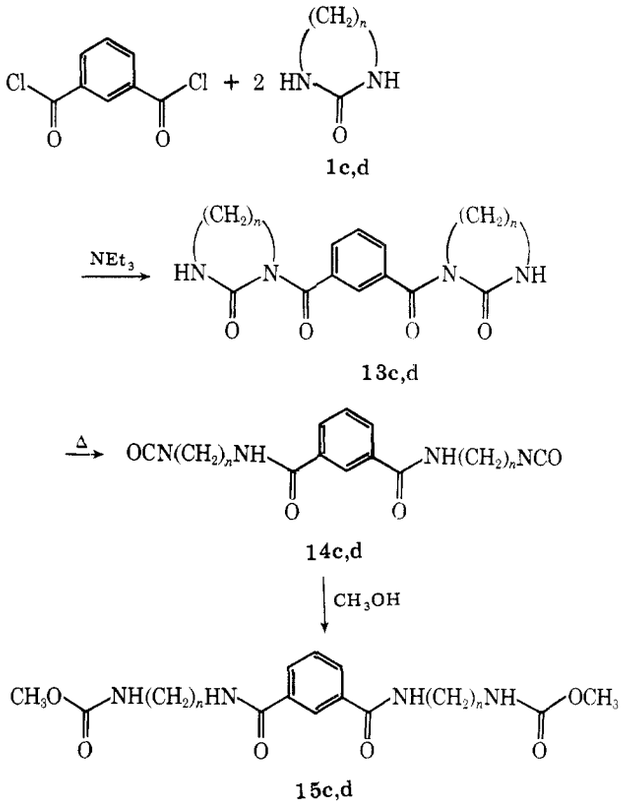
Attempts to prepare the urea **1d** from other O-acylated derivatives of **8** via Lossen degradation failed: Methyl chloroformate and phosgene treatment of **8** lead to **11** and **12**, respectively, but both compounds were hydrolyzed back to the amide oxime **8** on treatment with dilute aqueous base.

As a model for a polymer system, isophthaloyl chloride was reacted with 2 equiv of **1c** or **1d** to give the bisurea derivatives **13c** and **13d.** Heating of **13** in *o*-dichlorobenzene produces the diisocyanates **14c** and **14d,** as evidenced by infrared spectroscopy and trapping with methanol to give the biscarbamates **15c** and **15d.** Heating of **13c** or **13d** in methanol did not produce **15,** indicating that this difunctional monomer is stable in alcohol (Scheme III).

Scheme II



Scheme III



The formation of polyurethanes from **13** and suitable polyols will be the subject of a forthcoming paper.

Experimental Section[7]

Perhydro-1,3-diazepin-2-one (Tetramethyleneurea) (1c). To 88 g (1 mol) of tetramethylenediamine in a mixture of 250 mL of ethanol and 250 mL of water, 62.5 g (1.04 mol) of carbonyl sulfide gas was added with stirring over a period of 80 min. The temperature rose from 32 to 45 °C during the addition and the salt formed in the reaction precipitated after the addition was completed. The reaction mixture was heated to 60 °C and 8 mL of concentrated HCl was added dropwise over a period of 3 min. The reaction mixture was then heated at 73–83 °C for 3 h, during which time hydrogen sulfide evolved and the precipitated salts went into solution. The solution was cooled and extracted with hot chloroform using a liquid–liquid continuous extractor. Evaporation of the chloroform yielded 77.1 g of the crude urea, mp 157–164 °C. Sublimation at 150–190 °C (0.1 mm) afforded 67 g (59%) of **1c,** mp 166–170 °C (lit.[4] mp 172 °C).

1-Benzoylperhydro-1,3-diazepin-2-one (1-Benzoyltetramethyleneurea) (2c). To a mixture of 5.7 g (0.05 mol) of tetramethyleneurea **1c** and 7.6 g (0.075 mol) of triethylamine in 200 mL of ethylene dichloride, 7 g (0.05 mol) of benzoyl chloride was added dropwise over a period of 10 min at 82–85 °C with stirring. The reaction mixture was refluxed for 90 min. Cooling to room temperature and filtration yielded 11.3 g of a mixture of amine hydrochloride salts and benzoyltetramethyleneurea. Trituration of the 11.3 g in 100 mL of water and filtration afforded 5.85 g of benzoyltetramethyleneurea, mp 207–208 °C. Ethylene dichloride was removed from the first filtrate by evaporation, and the 7.25-g residue obtained was triturated in water. Filtration afforded an additional 2.7 g of product, mp 182–192 °C. The total yield was 8.55 g (78%).

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.46; N, 12.83. Found: C, 65.98; H, 6.29; N, 13.02.

Methyl 4-Benzoylamidobutylcarbamate (4c). A solution of 0.5 g (0.0023 mol) of *N*-benzoyltetramethyleneurea (**2c**) in 20 mL of *o*-dichlorobenzene was refluxed for 2 h and, after cooling to 65 °C, 1.0 g of methanol was added. Short heating converted all of the generated isocyanate into the carbamate as evidenced by infrared spectroscopy. On cooling, 0.35 g (61%) of methyl 4-benzoylamidobutylcarbamate (**4c**), mp 126–127 °C, was obtained.

Anal. Calcd for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.24; N, 11.19. Found: C, 62.18; H, 6.97; N, 10.91.

3,4,5,6-Tetrahydro-7-methoxy-2*H*-azepine (**7**) was obtained

in 65–70% yield on treating a suspension of the hydrochloride of 3,4,5,6-tetrahydro-7-chloro-2*H*-azepine[3] in carbon tetrachloride with excess methanol. Removal of solvent and excess methanol in vacuo leaves a thick oil, which is treated with a saturated Na_2CO_3 solution. Extraction of the aqueous phase with methylene chloride and vacuum distillation of the liquid residue, left after evaporating the solvent, gave **7**, bp 60–61 °C (20 mm) (lit.[8] bp 65–67 °C at 24 mm).

Hexahydro-2*H*-azepin-2-one oxime (ε-Caprolactam Oxime) (8) was prepared in nearly quantitative yield by following a literature procedure and reacting equivalent amounts of **7** and hydroxylamine hydrochloride in refluxing methanol in the presence of excess $NaHCO_3$ as hydrogen chloride scavanger; mp 169–170 °C (lit.[4] mp 166 °C).

Hexahydro-2*H*-azepin-2-one (*O*-Methylsulfonyl)oxime (9). To an ice-cooled suspension of 5.20 g (0.04 mol) of oxime **8** in 30 mL of pyridine was added dropwise 4.5 g (0.04 mol) of methanesulfonyl chloride. A light-tan solution was formed from which colorless crystals of pyridinium chloride precipitated toward the end of the addition. After additional cooling for 2 h, most of the solvent was removed in vacuo, and the remaining oily residue was triturated with 20–30 mL of water, causing separation of colorless crystals. Filtration and ice-water washings left 7.6 g (90%) of **9**, mp 89–90 °C.

Anal. Calcd for $C_7H_{14}N_2O_3S$: C, 40.77; H, 6.84; N, 13.59. Found: C, 40.92; H, 7.04; N, 13.70.

Perhydro-1,3-diazocin-2-one (1d). A suspension of 7.6 g (0.037 mol) of mesylate **9** in a sodium hydroxide solution (2.5 g of NaOH in 50 mL of water) was stirred at room temperature for 2 h. The starting material dissolves slowly, and toward the end of the reaction colorless crystals of the urea started to precipitate. The newly formed suspension was transferred to a liquid–liquid extractor and extracted with refluxing chloroform for 2 h. The dried extract was evaporated to dryness, leaving colorless crystals of **1d:** 4.5 g (95%); mp 240–245 °C; identical in IR comparison with an authentic sample.[4]

Hexahydro-2*H*-azepin-2-one (*O*-Methoxycarbonyl)oxime Hydrochloride (11). Heating a suspension of 2.6 g (0.02 mol) of oxime **8** in 20 mL of chloroform with 4.0 g of methyl chloroformate for 4 h converted the starting material into a voluminous precipitate. Filtration and washing with chloroform leaves 3.30 g (75%) of **11**, mp 158–160 °C, with loss of hydrogen chloride.

Anal. Calcd for $C_8H_{15}ClN_2O_3$:[9] C, 43.15; H, 6.79; N, 12.58. Found: C, 42.38; H, 6.88; N, 12.29.

Treatment of **11** with NaOH–H_2O as described for the conversion of **9** into **10** resulted in the recovery of amide oxime **8**, as evidenced by IR comparison with authentic material.

3a,4,5,6,7,8-Hexahydro-3*H*-2,1,3a-oxidazolo[3,4-*a*]azepin-3-one (12). Solid amide oxime **8** (12.8 g, 0.1 mol) was added in small portions to a cold solution of 30 g (0.3 mol) of phosgene in 100 mL of benzene. The obtained suspension was heated to reflux for 3 h, during which time the starting material dissolved. Cooling of the obtained solution and concentrating in vacuo gave an amber oil, which solidifed on standing. Treatment with water and filtration afforded 11.8 g (76%) of **12**, mp (from H_2O) 40–41 °C; colorless needles; IR (KBr) 1765 cm^{-1} C=O).

Anal. Calcd for $C_7H_{10}N_2O_2$: C, 54.53; H, 6.54; N, 18.17. Found: C, 54.46; H, 6.38; N, 18.11; mol wt 146 (vapor pressure osmometric in $CHCl_3$).

Treatment of **12** with concentrated (50%) or diluted sodium hydroxide solution yielded only amide oxime **8** and no urea **10**.

1-Benzoylperhydro-1,3-diazocin-2-one (*N*-Benzoylpentamethyleneurea) (2d). To 2.56 g (0.02 mol) of pentamethyleneurea and 3.03 g (0.03 mol) of triethylamine in 100 mL of ethylene dichloride at reflux, 2.81 g (0.02 mol) of benzoyl chloride was added dropwise with stirring. Cooling and filtration afforded 1.85 g of triethylamine hydrochloride. The solvent was removed from the filtrate by evaporation, affording a 7.1-g residue. The residue was triturated with 200 mL of ethyl acetate and filtered, yielding 0.8 g of a mixture of amine hydrochloride and pentamethyleneurea. Evaporation of the filtrate yielded 4.3 g (92%) of *N*-benzoylpentamethyleneurea, mp 150–152 °C.

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.96, N, 12.06. Found: C, 67.45; H, 7.02, N, 12.21.

Methyl 5-Benzoylamidopentylcarbamate (4d). A solution of 0.5 g (0.0021 mol) of *N*-benzoylpentamethyleneurea (**2d**) in 20 mL of *o*-dichlorobenzene was refluxed for 4 h. After cooling to 85 °C, a total of 1.0 g of methanol was added and the solution was refluxed for another hour. Evaporation of the solvent and excess methanol and trituration of the residue with water yielded 0.3 g (52%) of **4d,** mp 75–78 °C.

Anal. Calcd for $C_{14}H_{20}N_2O_3$: C, 63.61; H, 7.62; N, 10.59. Found: C, 63.58; H, 7.52; N, 10.53.

1,1′-Isophthaloylbis(perhydro-1,3-diazepin-2-one) (13c). To 22.8 g (0.2 mol) of tetramethyleneurea (**1c**) in 400 mL of ethylene dichloride, 20.3 g (0.1 mol) of isophthaloyl chloride in 150 mL of ethylene dichloride was added dropwise with stirring over a period of 33 min. The temperature rose from 21 to 26 °C and a precipitate formed during the addition. The reaction mixture was stirred at room temperature for 1 h after which 22.2 g (0.22 mol) of triethylamine in 30 mL of ethylene dichloride was added dropwise with stirring over a period of 35 min. The temperature rose from 24 to 34 °C during the addition. The reaction mixture was heated to 51 °C and then cooled to below 10 °C. Filtration yielded 46.45 g of a mixture of triethylamine hydrochloride and product. Washing in water and filtration afforded 22.8 g (64%) of **13c,** mp 238–240 °C. An additional 1.3 g (3.6%) of **13c** was recovered from the ethylene dichloride filtrate.

Anal. Calcd for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.29; H, 6.21; N, 15.53.

Bis[(4-Methoxycarbamoyl)butyl]isophthalamide (15c). A solution of 2.5 g (7.0 mmol) of **13c** in 50 mL of *o*-dichlorobenzene was refluxed for 4.5 h. The solution was cooled to room temperature and 4 mL of methanol was added. Heating at 80–85 °C converted all the generated isocyanate into the carbamate, as evidenced by infrared spectroscopy. The product precipitated on cooling and was separated from the solvent by filtration. Trituration with chloroform and filtration yielded 1.2 g (42%) of **15c,** mp 179–180 °C (water).

Anal. Calcd for $C_{20}H_{30}N_4O_6$: C, 56.86; H, 7.16; N, 13.26. Found: C, 56.80; H, 7.40; N, 13.15.

1,1′-Isophthaloylbis(perhydro-1,3-diazocin-2-one) (13d). To a suspension of 25.6 g (0.2 mol) of pentamethyleneurea (**1d**) in 200 mL of 1,2-dichloroethane is added dropwise with stirring a solution of 20.3 g (0.1 mol) of isophthaloyl chloride in 100 mL 1,2-dichloroethane. The starting material is slowly dissolved, but a new precipitate is formed at the same time. The resulting thick mixture is kept for 18 h at room temperature after which 20.0 g (0.2 mol) of triethylamine is added gradually and the temperature is raised to ca. 70 °C. Most of the precipitate dissolves within 2–3 h, leaving only triethylamine hydrochloride undissolved. Filtration of the hot solution affords 18.40 g of triethylamine hydrochloride, and evaporation of the filtrate yields a colorless residue which after stirring with 200 mL of water for 30 min, filtration, and water washing leaves 31.40 g (81%) of **13d,** mp 183–184 °C; further purification by recrystallization from isopropyl alcohol.

Anal. Calcd for $C_{20}H_{26}N_4O_4$: C, 62.16; H, 6.78; N, 14.50. Found: C, 62.10, H, 6.93; N, 14.42.

Bis[(5-methoxycarbamoyl)pentyl]isophthalamide (15d). A solution of 1.0 g (1.03 mmol) of crude **13d** in 5 mL of *o*-dichlorobenzene was refluxed for 1.5 h. After cooling to room temperature, 10 mL of methanol was added and the reaction mixture was heated at 80–90 °C for 1 h. Complete conversion of the generated isocyanate to the carbamate was evidenced by infrared spectroscopy (disappearance of NCO). Solvent and excess methanol were removed by vacuum distillation; the oily residue was taken up in methanol. Diluting with water caused slow precipitation of colorless crystals which were filtered off after standing for 24 h: 0.6 g (52%) of **15d,** mp 144–145 °C (2-propanol–water).

Anal. Calcd for $C_{22}H_{34}N_4O_6$: C, 58.65; H, 7.61; N, 12.43. Found: C, 58.51; H, 7.75; N, 12.38.

Registry No.—**1,** 19055-93-7; **1d,** 5700-13-0; **2c,** 65252-81-5; **2d,** 54236-70-3; **4c,** 65252-82-6; **4d,** 65252-83-7; **8,** 19214-08-5; **9,** 65252-84-8; **11,** 65252-85-9; **12,** 65252-86-0; **13c,** 65252-87-1; **13d,** 65252-88-2; **15c,** 65252-89-3; **15d,** 65252-90-6; benzoyl chloride, 98-88-4; isophthaloyl chloride, 99-63-8.

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