OPTICALLY ACTIVE HEPTAMETHYLENECARBODIIMIDE*

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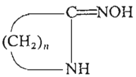
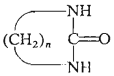
Heptamethylenecarbodiimide *III* ($n = 7$) and undecamethylenecarbodiimide *III* ($n = 11$) were prepared. The former was partly resolved into its optical antipodes by chromatographic treatment on a column of partially acetylated cellulose.

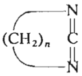
In one of our previous papers[1] we have reported on the resolution of (R,S)-N,N'-bis-α-phenylethylcarbodiimide into its optical antipodes by chromatographic treatment on partially acetylated cellulose. Now we have attempted to resolve into the optical antipodes some cyclic carbodiimides. The starting materials for their preparation were 8-octanelactam and 12-dodecanelactam, which were converted *via* S-methyl-8-octenethiolactim of O-methyl-12-dodecenelactim to 8-octanelactamoxime *I* ($n = 7$) and 12-dodecanelactamoxime *I* ($n = 11$), respectively. These substances were further rearranged with polyphosphoric acid to heptamethyleneurea *II* ($X = O$, $n = 7$) and undecamethyleneurea *II* ($X = O$, $n = 11$), which with phosphorus pentasulfide afforded the sulfur analogues *II* ($X = S$, $n = 7, 11$). These were oxidized with mercuric oxide to heptamethylenecarbodiimide *III* ($n = 7$) and undecamethylenecarbodiimide *III* ($n = 11$). Heptamethylenecarbodiimide was chromatographed on a column of partially acetylated cellulose and the (−)-antipode, whose ORD curve possesses a positive shape, was obtained; $[\alpha]^{20}_{365}$ −2·79°C (cyclohexane). Attempts to resolve in this manner undecamethylenecarbodiimide into its optical antipodes failed; the fourteen-membered ring, owing to its enhanced mobility, obviously enables the carbodiimide grouping to racemize rapidly.



I



II
($X = O, S$)



III

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EXPERIMENTAL

The samples to be analyzed were dried for 6 h at room temperature in the vacuum of an oil vacuum pump. The ORD curves were measured on an instrument Jasco UV 5. The melting and boiling points have not been corrected.

Heptamethylenecarbodiimide *III* ($n = 7$)

8-Octanelactam was converted on the action of phosphorus pentasulfide to 8-octanethiolactam[2] (75%), m.p. 84—86°C, affording on the methylation with dimethyl sulfate S-methyl-8-octenethiolactim (85%), b.p. 78—80°C/26·6 Pa. The reaction of the latter with hydroxylamine gave 8-octanelactamoxime *I* ($n = 7$) (55%), m.p. 118—119°C, rearranged by polyphosphoric acid[3] to heptamethyleneurea *II* (X = O, $n = 7$) (33%), m.p. 164—165°C, from which heptamethylenethiourea *II* ($X = S$, $n = 7$), m.p. 159—160°C, was prepared (45%) on the action of phosphorus pentasulfide. To a solution of heptamethylenethiourea (87 mmol) in 25 ml of dichloromethane, dry mercuric oxide (20·3 mmol) was added portionwise under shaking. After 16 h, mercuric sulfide was filtered off, the solution was dried with magnesium sulfate and evaporated. The residue was evaporated to obtain 0·87 g (72·5%) of the substance *III* ($n = 7$), b.p. 40—43°C/26·6 Pa. For $C_8H_{14}N_2$ (138·2) calculated: 69·52% C, 10·21% H, 20·27% N; found: 69·19% C, 10·33% H, 20·25% N.

Resolution of the Substance *III* ($n = 7$) into its Optical Antipodes

The substance *III* ($n = 7$) (0·2 g, 1·45 mmol) was chromatographed on a column of partially acetylated cellulose (200 g, acetylation degree 2·42). Cyclohexane served as the eluting agent, and 10 ml fractions were collected. The detection was accomplished on Silufol using iodine vapours. The first ten fractions were concentrated in vacuum at room temperature. The optical rotatory power was measured in a thermostatted 10 cm cell on an instrument Perkin–Elmer 141 MS with the precision of 0·002°. $[\alpha]_{365}^{20}$ —2·79° (*c* 0·72, cyclohexane). The solution racemized completely during 8 hours's standing. The higher fractions from the chromatographic treatment did not exhibit optical activity.

12-Dodecanelactamoxime *I* ($n = 11$)

12-Dodecanelactam, m.p. 150—153°C, afforded O-methyl-12-dodecenelactim (78%), b.p. 75 to 80°C/40 Pa, on the methylation with dimethyl sulfate[4]. O-methyl-12-dodecenelactim (275 mmol) was boiled with a mixture of hydroxylamine hydrochloride (280 mmol) and sodium hydrogencarbonate (281 mmol) in 250 ml of methanol for 3 h. After evaporation, the residue was extracted with ether in a Soxhlet apparatus. The 12-dodecanelactamoxime (67%) was recrystallized from a mixture benzene–light petroleum. M.p. 126—127°C. For $C_{12}H_{14}N_2O$ (212·3) calculated: 67·88% C, 11·39% H, 13·19% N; found: 67·91% C, 11·39% H, 12·86% N.

Undecamethylenethiourea *II* (X = S, $n = 11$)

12-Dodecanelactamoxime (942 mmol) was added under stirring to 300 g of polyphosphoric acid heated to 135°C. After 2 hours heating the mixture was poured on ice and alkalized with sodium hydroxide to pH 8. The separated undecamethyleneurea (16·7 g, 83%) was recrystallized from ethanol. M.p. 198—199°C, according to[5] m.p. 192—194°C.

A mixture of undecamethylurea (94·2 mmol), magnesium oxide (372 mmol), phosphorus pentasulfide (180 mmol), and pyridine (600 ml) was boiled with stirring for 3 h. After evaporation, the residue was diluted with 200 ml of water and adjusted to pH 8 with sodium hydroxide. The product separated was extracted with 4 . 100 ml of chloroform. After evaporation of the chloroform, the product was crystallized from tetrachloromethane, with which it formed an adduct of the ratio approximately 6 : 1 (23·2 g, 98%), melting obviously after the liberation of the tetrachloromethane. For $(C_{12}H_{24}N_2S).CCl_4$ (1 524) calculated: 57·52% C, 9·52% H, 11·03% N, 12·62% S, 9·30% Cl; found: 57·44% C, 9·63% H, 11·33% N, 12·60% S, 8·80% Cl. The solvent was removed from the adduct in vacuum. M.p. 149·5—150°C. For $C_{12}H_{24}N_2S$ (228·4) calculated: 53·10% C, 10·59% H, 12·27% N, 14·04% S; found: 63·37% C, 10·89% H, 12·41% N, 13·82% S.

Undecamethylenecarbodiimide *III* ($n = 11$)

To a solution of the substance *II* (X = S, $n = 11$) in 80 ml of dichloromethane was added portionwise 55·4 mmol of yellow mercuric oxide within 2 h. After centrifugalization of the mercuric sulfide the filtrate was dried with anhydrous magnesium sulfate. The solvent was distilled off and the product was distilled in vacuum. The total of 1·8 g (42%) of the product boiling at 80 to 83°C/53·5 Pa was obtained. For $C_{12}H_{22}N_2$ (194·3) calculated: 73·66% C, 11·46% H, 14·93% N; found: 73·97% C, 11·43% H, 14·96% N. Only optically inactive material could be obtained on the chromatographic treatment of the product on a column of partially acetylated cellulose in the conditions applied to *III* ($n = 7$).

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