881. *The Action of Bases on Decamethylene Di-iodide.*

By E. P. TAYLOR.

When decamethylene di-iodide is heated with potassium carbonate, potassium hydroxide, and 95% ethanol, a mixture of 10-ethoxydec-1-ene, 1,10-diethoxydecane, 10-ethoxydecan-1-ol, and decane-1,10-diol is obtained. With ethanolic sodium ethoxide, decamethylene di-iodide gives only 10-ethoxydec-1-ene and 1,10-diethoxydecane. Some reactions of 10-ethoxydec-1-ene are described.

DURING unsuccessful attempts to prepare certain decamethylenebisquaternary derivatives of melamine, it was observed that when a mixture of decamethylene di-iodide, potassium carbonate and potassium hydroxide in 95% ethanol was heated under reflux for several days, a mixture of decane-1,10-diol, 10-ethoxydecan-1-ol, 1,10-diethoxydecane, and 10-ethoxydec-1-ene $EtO\cdot[CH_2]_8\cdot CH{:}CH_2$ (I) was obtained. Oxidation of the latter with diluted nitric acid yielded, not the expected azelaic acid, but suberic acid, although in poor yield. It was at first thought that azelaic acid might have been formed initially and have decomposed on further heating with nitric acid, since it has been reported [1] that higher dicarboxylic acids having an odd number of carbon atoms tend to break down into shorter dicarboxylic acids. However, when authentic azelaic acid was treated with diluted nitric acid under similar conditions, the major product was unchanged material (approximately 55%), together with some succinic acid and a small quantity of glutaric acid. It is possible that the mother-liquor contained a trace of suberic acid, but the amount was negligible. Since 1,10-diethoxydecane also gave suberic acid, not sebacic acid, on oxidation with diluted nitric acid, it seems that oxidation of this and of the unsaturated monoether must proceed *via* prior elimination of ethanol to yield terminal alkenes, rather than by cleavage of the ether links to primary alcohols.

When decamethylene di-iodide was heated under reflux with ethanolic sodium ethoxide the only products were 1,10-diethoxydecane and the unsaturated ether (I).

EXPERIMENTAL

All m. p.s are uncorrected.

Action of Potassium Carbonate–Potassium Hydroxide on Decamethylene Di-iodide.—A mixture of the di-iodide (236·4 g., 0·6 mole), anhydrous potassium carbonate (41·4 g., 0·3 mole), potassium hydroxide (98%, 34·3 g., 0·6 mole), and ethanol (95%, 2700 ml.) was heated under reflux for 300 hr. The solvent was then distilled off, sufficient water added to dissolve inorganic salts, and the mixture extracted with ether (2 × 500 ml.). The combined ether extracts were washed three times with saturated sodium thiosulphate solution dried ($CaSO_4$), and the solvent removed. The residue was then distilled *in vacuo*, the following fractions being collected: (i) <55°/0·25 mm., 12·6 g.; (ii) 56—78°/0·3 mm., 2·03 g.; (iii) 78—98°/0·3 mm., 65·2 g.; (iv) 100—120°/0·3 mm., 27·5 g. The residue was treated with excess of light petroleum (b. p. 40—60°), and crude decane-1,10-diol separated; this, after being filtered off, washed with light petroleum (b. p. 40—60°), and dried, had m. p. 68° (mixed m. p. with authentic material 71—72°) (1·91 g.).

Fraction (i), after two redistillations, gave 10-*ethoxydec*-1-*ene* (I) (10·6 g.), b. p. 42—44°/0·2 mm., n_D^{21} 1·4310 (Found: C, 78·1; H, 13·0; O, 8·8; OEt, 24·2%; *M*, 170. $C_{12}H_{24}O$ requires C, 78·3; H, 13·15; O, 8·7; OEt, 24·5%; *M*, 184).

Fraction (ii) was still unsaturated, and was rejected. Fraction (iii), on redistillation, gave material (12·51 g.), b. p. 72—80°/0·15—0·2 mm., which was rejected, and material (50·53 g.), b. p. 80—84°/0·2 mm. This fraction was heated over metallic sodium (*ca.* 2—3 g. in slices) in an oil-bath at 170° for 2 hr.; hydrogen was evolved, and a small quantity of white precipitate separated. After cooling, anhydrous ether was added, the mixture filtered, and the solvent removed. The residue on distillation *in vacuo* gave 1,10-diethoxydecane (45·2 g.), b. p. 76—77°/0·15 mm., n_D^{21} 1·4294, identical with a sample prepared by Egorova's method [2] (who gives b. p. 257—260°) (Found: C, 72·75; H, 13·2; O, 14·2; OEt, 39·1%; *M*, 206. Calc. for $C_{14}H_{30}O_2$: C, 73·0; H, 13·15; O, 13·9; OEt, 39·1%; *M*, 230).

Fraction (iv) was redistilled, the fraction of b. p. 93—100°/0·15 mm. (19·7 g.) being collected. This, on treatment with a solution of phenyl isocyanate (11·7 g.) in light petroleum (b. p. 40—60°; 30 ml.), gave an almost pure *phenylcarbamate* (18·0 g.), m. p. 56°. An analytical sample crystallised from aqueous ethanol as glistening plates, m. p. 57·5° (Found: C, 71·1; H, 9·7; N, 4·4. $C_{19}H_{31}NO_3$ requires C, 71·0; H, 9·7; N, 4·4%). A mixture of the phenylcarbamate, ethanol (90 ml.), water (15 ml.), and 5N-sodium hydroxide (30 ml.) was heated under reflux for 48 hr. Crystals which had separated were rejected, as much solvent as possible was distilled off on the water-bath, and the residue was diluted with water (45 ml.). The oil which separated was extracted with ether, the combined ether extracts were washed (thrice with N-H_2SO_4, twice with water) and dried ($CaSO_4$); the solvent was then removed and the residue distilled *in vacuo*. The fraction of b. p. 89—91°/0·17 mm. (8·7 g.) on redistillation yielded 10-*ethoxydecan*-1-*ol*, b. p. 91—92°/0·2 mm., n_D^{21} 1·4419 (Found: C, 70·95; H, 12·75; O, 16·0; OEt, 22·75%; *M*, 197. $C_{12}H_{26}O_2$ requires C, 71·3; H, 13·0; O, 15·8; OEt, 22·3%; *M*, 202) [3,5-*dinitrobenzoate*, cream-coloured needles, m. p. 46°, from aqueous ethanol (Found: C, 57·45; H, 6·9; N, 7·0. $C_{19}H_{28}N_2O_7$ requires C, 57·6; H, 7·1; N, 7·1%)].

Reactions of 10-*Ethoxydec*-1-*ene*.—(a) With bromine in carbon tetrachloride at 0°, 1,2-*dibromo*-10-*ethoxydecane* was obtained, b. p. 115°/0·15 mm., n_D^{21} 1·4880 (Found: C, 42·2; H, 7·15; O, 5·0; Br, 46·5; OEt, 13·4. $C_{12}H_{24}Br_2O$ requires C, 41·9; H, 7·0; O, 4·65; Br, 46·5; OEt, 13·1%).

(b) *Epoxidation with peractic acid.* Epoxidation by the general method of Findley, Swern, and Scanlan [3] gave 1,2-*epoxy*-10-*ethoxydecane*, b. p. 65—66°/0·1 mm., n_D^{20} 1·4368 (Found: C, 72·8; H, 12·0; O, 15·45; OEt, 22·2%; *M*, 194. $C_{12}H_{24}O_2$ requires C, 72·0; H, 12·1; O, 16·0; OEt, 22·5%; *M*, 200).

(c) *Oxidation with nitric acid.* A mixture of 10-ethoxydec-1-ene (1·0 g.), nitric acid (*d* 1·42, 20 ml.), and water (20 ml.) was heated under reflux in an oil-bath at 100°, and an initial fairly rapid evolution of oxides of nitrogen occurred. After 120 hours' heating as much solvent as possible was distilled off under reduced pressure (*ca.* 15—20 mm.), and the residue treated with twice its volume of water and stored overnight. The precipitate was then filtered off, washed with a little water, and dried, giving crude suberic acid (0·26 g.), softening at 126—128°, m. p. 132—133° (Found: C, 54·9; H, 7·9; O, 37·0. Calc. for $C_8H_{14}O_4$: C, 55·2; H, 8·1; O, 36·8%), which recrystallised from water as needles, m. p. and mixed m. p. with authentic suberic acid, 139°. Under identical conditions, 1,10-diethoxydecane (1·1 g.) gave 0·2 g. of crude suberic acid, m. p. 124—128° after previous sintering; the initial evolution of oxides of nitrogen was very vigorous. When azelaic acid (5·0 g., purified *via* the monomethyl ester) and nitric acid (100 ml. of *d* 1·42; in 100 ml. water) were heated together at 100° for 120 hr., there was only a slow evolution of gas. The solvent was removed *in vacuo*, hot water (10 ml.) added, and the mixture stored overnight and filtered. The product, after being washed with water and dried, was unchanged azelaic acid (2·80 g., 56%), m. p. and mixed m. p. 106°. The filtrate was concentrated to very small bulk and treated with an equal volume of hydrochloric acid, crude succinic acid (0·5 g.) being precipitated; it sintered at 151°, and became homogeneous at 174° (mixed m. p. with authentic acid, 179—181° after sintering at 174°). The mother-liquors were evaporated to dryness, and the residue (1·15 g.) was extracted with boiling benzene (50 ml.) and filtered hot. The insoluble residue was almost pure succinic acid (0·22 g.; m. p. 182—184° after sintering at 178°). The benzene filtrate was concentrated to small bulk, and allowed to crystallise. Repeated fractional crystallisations from benzene gave crude glutaric acid (0·06 g.) (sintered at 83—85° and slowly melted over a range; mixed m. p. 95° after sintering at 90°). All the benzene mother-liquors were then mixed and concentrated to about 2 ml. Paper chromatography of this, ninhydrin being used to locate the spots,[4] indicated the presence of succinic, glutaric, adipic, pimelic, suberic, and azelaic acids (cf. Cason, Fessenden, and Agre [5]).

---

[1] Selwitz and Whitaker, *J. Org. Chem.*, 1957, **22**, 1116.
[2] Egorova, *Zhur. fiz. Khim.*, 1910, **42**, 1655.
[3] Findley, Swern, and Scanlan, *J. Amer. Chem. Soc.*, 1945, **67**, 412.
[4] Long, Quayle, and Stedman, *J.*, 1951, 2197.
[5] Cason, Fessenden, and Agre, *Tetrahedron*, 1959, **7**, 289.

(d) *Oxidation with potassium permanganate.* A solution of 10-ethoxydec-1-ene (7·6 g.) in dry acetone (180 ml.) was heated to boiling under reflux, and the heating then discontinued. During the next 30 min., powdered potassium permanganate (18·1 g.) was added in small quantities at a rate sufficient to keep the mixture boiling. The mixture was then heated under reflux for 5 hr., and cooled, water (140 ml.) added, and the acetone removed at room temperature under reduced pressure. After the addition of sulphuric acid (25% v/v; 75 ml.), the manganese dioxide was reduced with sulphur dioxide. The resulting clear solution was then extracted repeatedly with ether, and the combined ether extracts were washed with water and then extracted with 10% sodium hydroxide solution (5 × 10 ml.). The alkaline extracts were mixed and washed once with ether. (All ether extracts were united and, after drying over $CaSO_4$, yielded 3·0 g. of crude unoxidised 10-ethoxydec-1-ene.) After acidification of the alkaline solution with dilute sulphuric acid, the oil which separated was extracted with ether, the ethereal extract dried ($CaSO_4$), the solvent recovered, and the residue distilled *in vacuo*. The fraction up to 120°/0·25 mm. (0·43 g.) was rejected; the fraction of b. p. 120—130°/0·25 mm. (2·12 g.) was redistilled, giving *ω-ethoxypelargonic acid* (1·65 g.), b. p. 113°/0·2 mm. (Found: C, 64·6; H, 10·7; OEt, 22·6%; equiv., 207. $C_{11}H_{22}O_3$ requires C, 65·35; H, 11·0; OEt, 22·3%; equiv., 202). On treatment of a solution of this acid in light petroleum (b. p. 40—60°) with *N*-phenylpiperazine,[6,7] an almost quantitative yield of the *salt* was obtained; this recrystallised from light petroleum (b. p. 40—60°) in glistening plates or flat needles, m. p. 40—42° (Found: C, 68·75; H, 9·65; N, 7·6. $C_{21}H_{36}N_2O_3$ requires C, 69·2; H, 10·0; N, 7·7%).

Alternative Synthesis of ω-Ethoxypelargonic Acid.—ω-Bromopelargonic acid [8] was converted into its ethyl ester (b. p. 94—95°/0·3 mm.); a solution of this ester (7·2 g.) in dry ethanol (10 ml.) was added during 30 min. to boiling ethanol (15 ml.) in which sodium (0·65 g.) had been dissolved. The mixture was then heated under reflux for a further 5 hr., and stored overnight. The bulk of the ethanol was then distilled off, and the residue cooled and poured into water containing a little dilute sulphuric acid. The oil which separated was extracted with ether, the extract washed with water and dried ($CaSO_4$), the ether removed, and the residue distilled *in vacuo*. The main fraction, b. p. 90—94°/0·3 mm. (4·1 g.), was redistilled, giving *ethyl ω-ethoxypelargonate*, b. p. 83—84°/0·35 mm. (Found: OEt, 39·9. $C_{13}H_{26}O_3$ requires OEt, 39·1%). Alkaline hydrolysis of this ester (2·0 g.) gave ω-ethoxypelargonic acid (1·15 g.), b. p. 106—107°/0·08 mm. (Found: OEt, 22·9%; equiv., 199); *N*-phenylpiperazine salt, m. p. and mixed m. p. 40—42°.

Synthesis of 10-*Ethoxydecan*-1-*ol*.—*Method* (*i*). ω-Bromodecanoic acid [8] was converted into its ethyl ester (b. p. 104—105°/0·35 mm.); a solution of this ester (11·4 g.) in dry ethanol (10 ml.) was then allowed to react with sodium ethoxide [from sodium (1·0 g.)] in dry ethanol (20 ml.) as described above for the pelargonic homologue. *Ethyl ω-ethoxydecanoate* (6·1 g.) had b. p. 90—92°/0·3 mm., n_D^{21} 1·4327 (Found: C, 68·9; H, 11·25; O, 19·9; OEt, 36·7. $C_{14}H_{28}O_3$ requires C, 68·85; H, 11·6; O, 19·7; OEt, 36·9%).

Sodium (4·25 g.) was heated with stirring under boiling dry toluene (10 ml.) until molten, and the stirring and heating were then stopped. A hot solution (*ca.* 80°) of ethyl ω-ethoxydecanoate (5 g.) in dry butanol (70 ml.; 0·002% of water) was run in rapidly; a vigorous reaction started. Heat was applied initially to maintain the reaction, and then discontinued. After *ca.* 1 hr., the mixture was heated under reflux with stirring for 2 hr. and then cooled. Water (5 ml.) was added cautiously, and the mixture heated for a further 1 hr. It was then cooled, water (10 ml.) was added, and the butanol layer was separated and dried (Na_2SO_4). After removal of the solvent, the bulk of the residue was twice distilled; 10-ethoxydecan-1-ol (1·7 g.) had b. p. 99—100°/0·4 mm. (phenylcarbamate, m. p. and mixed m. p. 57°).

Method (*ii*). Sodium (2·0 g.) was dissolved in anhydrous ethanol (40 ml.). To this was added a solution of 10-chlorodecan-1-ol [9] (15 g.) in anhydrous ethanol (40 ml.), and the mixture was heated under reflux for 40 hr. The solvent was then distilled off, the residue dissolved as far as possible in wet ether, and the ethereal extract dried (Na_2SO_4). After removal of the solvent, the residue was distilled *in vacuo*: the main fraction (10·75 g.; b. p. 103—107°/0·3 mm.) was crude 10-ethoxydecan-1-ol, and yielded almost pure phenylcarbamate (15·1 g.), m. p. 55—57° without recrystallisation.

---

[6] Pollard and MacDowell, *J. Amer. Chem. Soc.*, 1934, **56**, 2199.
[7] Pollard and Gidwani, *J. Org. Chem.*, 1957, **22**, 992.
[8] Chuit and Hausser, *Helv. Chim. Acta*, 1929, **12**, 463.
[9] Perrine, *J. Org. Chem.*, 1953, **18**, 1356.

Action of Sodium Ethoxide on Decamethylene Di-iodide.—Sodium (15·33 g., 0·67 mole) was dissolved in anhydrous ethanol (500 ml.), and decamethylene di-iodide (131·3 g., 0·33 mole) added. The mixture was heated under reflux for 80 hr., and the ethanol then distilled off; any unchanged sodium ethoxide was decomposed by addition of water, and the residue was extracted with ether. After the extract had been dried ($CaSO_4$), the ether was recovered, and the residue distilled *in vacuo*, giving three fractions, (*a*) b. p. 63—73°/0·45 mm. (19·4 g.), (*b*) b. p. between 73°/0·45 mm. and 82°/0·3 mm. (2·5 g.), and (*c*) b. p. 82—88°/0·3 mm. (43·6 g.). There was practically no residue. Fraction (*a*) on redistillation gave 10-ethoxydec-1-ene (17·1 g.), b. p. 44—46°/0·2 mm. (Found: C, 78·2; H, 12·9; O, 8·9; OEt, 24·2. Calc. for $C_{12}H_{24}O$: C, 78·3; H, 13·15; O, 8·7; OEt, 24·5%). Fraction (*b*) was rejected, and fraction (*c*), on redistillation, gave 1,10-diethoxydecane (40·3 g.), b. p. 82—84°/0·2 mm. (Found: C, 73·1; H, 12·95; O, 14·0; OEt, 38·4. Calc. for $C_{14}H_{30}O_2$: C, 73·0; H, 13·15; O, 13·9; OEt, 39·1%).

Research Division, Allen and Hanburys Ltd.,
Ware, Herts.

[*Received, April* 26*th*, 1960.]