952. *Alkenylation with Lithium Alkenyls. Part XV.* The Formation and Some Reactions of* 1-cyclo*Decenyl-lithium.*

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1-Chloro*cyclo*decene could not be induced to react with lithium, but 1-bromo*cyclo*decene is readily metallated. 1-*cyclo*Decenyl-lithium undergoes carboxylation to give *cyclo*dec-1-enecarboxylic acid, but reactions with other carbonyl compounds proceed abnormally.

MANY of the " non-classical " phenomena associated with " medium-sized " rings are at their height in the *cyclo*decane series [1] and an extension of earlier work [2] to the study of *cyclo*decenyl derivatives was therefore of interest.

The most convenient entry to the *cyclo*decane series is the acyloin condensation of the sebacic esters developed by Prelog and his co-workers.[3] By their procedures, with minor modifications described in the Experimental section, sebacoin can be obtained consistently in 60—65% yields and converted into *cyclo*decanone. Reaction of the latter with phosphorus pentachloride gave 1-chloro*cyclo*decene,[4] but the chloride could not be metallated by lithium under the conditions successfully employed for the lower homologues. A similar lack of reactivity has been observed with other *cyclo*decane derivatives, *e.g.*, in the formation of Grignard reagent from 1-bromo*cyclo*decane,[5] and is probably caused by steric factors which will be accentuated in heterogeneous reactions at metal surfaces.

Attention was next directed to 1-bromo*cyclo*decene, since a markedly greater reactivity of the bromo- over the chloro-*cyclo*alkene was observed in the *cyclo*octene series.[2] *cyclo*-Decanone was reduced to *cyclo*decanol which was dehydrated to a mixture of *cis*- and *trans*-*cyclo*decene,[4, 6, 7] and this mixture was treated with bromine in chloroform. Unlike the case of *cyclo*octene,[2] appreciable evolution of hydrogen bromide (presumably due to allylic bromine-substitution) was observed and a mixture was obtained from which a solid 1 : 2-dibromo*cyclo*decane was isolated in small yield. Attempts to convert *cyclo*decane-1 : 2-diol into the dibromide by phosphorus tribromide, or by hydrogen bromide in acetic acid, also met with little success; the *cis*-diol gave 1-acetoxy-2-bromo*cyclo*decane while the *trans*-diol did not react.

A method different from that employed for the lower homologues was therefore used. Sebacoin was converted via *cyclo*decanedione into *cyclo*decyne.[3, 4] The latter readily added hydrogen bromide, giving the desired 1-bromo*cyclo*decene, which should be the *trans*-ring isomer if the addition proceeds *trans*. In *cyclo*decene itself, the *cis*- and *trans*-ring isomers are of comparable stability, but the relative stability of the *trans*-configuration will, of course, be considerably reduced in 1-substituted derivatives owing to interference between the ring and an " inside " substituent; a model of *trans*-1-bromo*cyclo*decene exhibits appreciable steric strain. The infrared spectra are inconclusive, so that the stereochemistry of the bromide is uncertain though a *cis*-configuration or a mixture of geometrical isomers appears the more likely, particularly in view of the ready conversion into the lithium alkenyl described below.

1-Bromo*cyclo*decene underwent metallation by lithium exothermally and rapidly in ether. Carboxylation gave *cyclo*dec-1-enecarboxylic acid in low yield; the crude product

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* Part XIV, preceding paper.

[1] Prelog, *J.*, 1950, 420; Prelog and Schenker, *Helv. Chim. Acta*, 1952, **35**, 2044.

[2] Part XIV, preceding paper.

[3] Prelog *et al.*, *Helv. Chim. Acta*, 1947, **30**, 1741; 1952, **35**, 1598; cf. Brown and Borkowski, *J. Amer. Chem. Soc.*, 1952, **74**, 1894.

[4] Blomquist, Burge, and Suesy, *J. Amer. Chem. Soc.*, 1952, **74**, 3636.

[5] Ruzicka, Barman, and Prelog, *Helv. Chim. Acta*, 1951, **34**, 401.

[6] Cope, McLean, and Nelson, *J. Amer. Chem. Soc.*, 1955, **77**, 1628.

[7] Braude and Timmons, *J.*, 1950, 2000; Braude and Coles, *J.*, 1952, 1425; Dreiding and Pratt, *J. Amer. Chem. Soc.*, 1954, **76**, 1902.

had a wide m. p. range (70—115°) possibly indicative of a mixture of isomers, but a single crystallisation gave a sharp-melting acid, m. p. 130—131°, which showed ultraviolet and infrared absorption typical of an αβ-ethylenic acid ($\lambda_{max.}$ 2230 Å, $\nu_{max.}$ 1660 and 1625 cm.$^{-1}$) and was presumably the *cis*-isomer. Its constitution was confirmed by catalytic hydrogenation which afforded *cyclo*decanecarboxylic acid, identical with an authentic specimen [5] kindly provided by Professor V. Prelog.

The reactions of the lithium alkenyl with other carbonyl compounds were abnormal. Thus, with benzaldehyde small and variable yields of material having the composition of the expected alcohol were obtained, but the main product was a hydrocarbon, $C_{20}H_{34}$. This showed no intense ultraviolet absorption above 2100 Å and was not hydrogenated in acetic acid in the presence of platinic oxide, though unsaturation was indicated by rapid reaction with bromine. It seems probable that the hydrocarbon is di(*cyclo*dec-1-enyl), formed by a Wurtz coupling of the lithium alkenyl with unchanged bromide. Analogous side-reactions have also been observed with di- and tri-methylvinyl bromide,[7, 8] though not with 1-bromo*cyclo*octene,[2] and it is of interest that di(*cyclo*decyl) is one of the side products in the reactions of *cyclo*decylmagnesium bromide.[5] The resistance of di(*cyclo*decenyl) to catalytic hydrogenation is not unexpected since *cyclo*decene is not reduced under comparable conditions, and the absence of ultraviolet light absorption characteristic of a conjugated system may similarly be ascribed to steric hindrance [9] since models show that the two double bonds cannot be coplanar.

EXPERIMENTAL

Analytical data were determined in the organic microanalytical (Mr. F. H. Oliver and staff) and spectroanalytical (Mr. R. L. Erskine and Mrs. A. I. Boston) laboratories of this Department.

2-*Hydroxy*cyclo*decanone* (*Sebacoin*).—The following procedure, based on the method of Prelog *et al.*,[3] consistently gave yields of 60—65% from dimethyl, diethyl, or dibutyl sebacate. Xylene (2 l.) was distilled into a special, 2 l. round-bottomed flask with a wide (4·5 × 14 cm.) neck fitted with an external water-condenser and a B 45 ground-glass joint. 500 Ml. of xylene were distilled out of the flask, which was heated by an electric mantle, to remove last traces of moisture. Clean sodium pieces (46 g.) were added, and then a stainless-steel head, provided with two side-inlets and a central stirrer running on two internal ball-bearings, driven by a 1/3 h.p. electric motor and fitted with a 1·5 × 13 cm. stainless-steel spiral which scraped the bottom of the flask, was placed in position. A slow stream of oxygen-free nitrogen was passed into the flask and the heating was adjusted so that the xylene refluxed *gently* in the condenser-neck of the flask (if boiling was too vigorous and xylene vapour reached the cone of the steel head, the expansion of the latter cracked the flask). About 1 hr. after correct running conditions had been attained, sebacic ester (1 mol.) in xylene (100 ml.) was added at an even rate during 15 hr. through a finely adjusted dropping funnel. After a further hour's stirring the steel head was replaced by a simple glass head and, while the passage of nitrogen was continued, the flask was cooled in ice-salt, and methanol (10 ml.) was added, followed by 50% sulphuric acid (200 ml.). The sodium sulphate was filtered off and the xylene layer was separated, washed with water, sodium carbonate solution, and again with water, dried (Na_2SO_4), and distilled, giving crude sebacoin (51—55 g.), b. p. 100—110°/1 mm., which solidified and was used without further purification.

cyclo*Decanone*.—Reduction of sebacoin by the method of Prelog *et al.* was found to be highly dependent on the batch of zinc powder used, as has been noted by others.[3, 4] Effective batches were selected by carrying out small-scale experiments and estimating the *cyclo*decanone as semicarbazone. The following procedure was used. Sieved zinc powder (11·6 g.) followed by concentrated hydrochloric acid (6·6 g.) was added, with vigorous stirring, to a solution of sebacoin (4·6 g.) in acetic acid (11·6 ml.) in a 250 ml. flask. The mixture was heated to 130° and two further portions of hydrochloric acid (6·6 ml.) were added at intervals of 30 min. The solution was decanted from unchanged zinc, diluted with water (100 ml.), and extracted with ether. The ether extract was washed with sodium carbonate and the solvent was distilled off.

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[8] Braude and Evans, *J.*, 1955, 3331.

[9] Cf. Braude, *Experientia*, 1955, **11**, 457.

The residue was treated with aqueous semicarbazide acetate, giving *cyclo*decanone semicarbazone (3·6 g., 56%), m. p. 200°. The ketone, b. p. 103—104°/10 mm., n_D^{18} 1·4825, was regenerated by steam-distillation of the semicarbazone with twice its weight of phthalic anhydride.

A solution of the ketone (4·6 g.) and benzaldehyde (3·2 g.) in aqueous ethanol–1M-potassium hydroxide (20 ml.) was kept at room temperature for 24 hr. The product was isolated with ether and distilled from naphthalene-β-sulphonic acid, giving: (i) 2-*benzylidene*cyclo*decanone* (1·0 g.), b. p. 70°/10^{-4} mm., n_D^{23} 1·5780 (Found: C, 84·3; H, 9·3. $C_{17}H_{22}O$ requires C, 84·25; H, 9·15%), characterised by a red 2 : 4-*dinitrophenylhydrazone* which after chromatography in benzene on alumina and crystallisation from methanol–ethyl acetate had m. p. 143—144° (Found: C, 65·5; H, 6·4; N, 13·3. $C_{23}H_{26}O_4N_4$ requires C, 65·4; H, 6·2; N, 13·3%); (ii) 2 : 10-*dibenzylidene*cyclo*decanone* (80 mg.) which after crystallisation from pentane had m. p. 150—151° (Found: C, 86·9; H, 8·1. $C_{24}H_{26}O$ requires C, 87·2; H, 7·9%). The monobenzylidene derivative is semisolid at room temperature and appears to be a mixture of *cis*- and *trans*-isomers; when melted by warming to 25°, it had $\lambda_{max.}$ 2700 and 2800 Å (ε 21,000 and 18,000 respectively) in hexane, while if completely solidified by cooling below 15° it had $\lambda_{max.}$ 2700 and 2800 Å (ε 9500 and 7000 respectively) in hexane. The dibenzylidene derivative had $\lambda_{max.}$ 2270, 2510, 2660, and 2800 Å (ε 8000, 8000, 10,500, and 8500 respectively).

1-*Chloro*cyclo*decene*.—*cyclo*Decanone (5·1 g.) in benzene (15 ml.) was added, with stirring, to phosphorus pentachloride (21 g.). The mixture was kept at room temperature for 24 hr., then poured into 10% aqueous sodium carbonate (100 ml.). The solution was extracted with benzene, and the extract was dried (Na_2SO_4) and distilled, giving 1-chloro*cyclo*decene, b. p. 110°/12 mm., n_D^{26} 1·5010 (Found: C, 69·4; H, 9·9; Cl, 20·5. Calc. for $C_{10}H_{17}Cl$: C, 69·55; H, 9·9; Cl, 20·6%). (Blomquist *et al.*[4] give b. p. 121—124°/29 mm., n_D^{20} 1·5038.)

No appreciable reaction could be induced between the chloride and lithium metal in ether, even after refluxing for 24 hr.

1 : 2-*Dibromo*cyclo*decane*.—*cyclo*Decanone (21 g.) was reduced with lithium aluminium hydride (1·8 g.) in boiling ether (150 ml.) to *cyclo*decanol (21 g.), b. p. 129°/16 mm., n_D^{20} 1·4920. This was dehydrated at 250—280° with naphthalene-β-sulphonic acid (0·4 g.) to *cyclo*decene (15 g.), b. p. 74—76°/15 mm., n_D^{18} 1·4829, the infrared spectrum of which showed it to consist of approximately equal proportions of *cis*- and *trans*-isomers (cf. ref. 4).

Bromine (4·0 g.) in chloroform (10 ml.) was added dropwise to *cyclo*decene (3·7 ml.) in chloroform (5 ml.) at 0° under nitrogen. Appreciable evolution of hydrogen bromide was observed. Distillation gave a range of fractions (1·3 ml.), b. p. 110—128°/10^{-3} mm., n_D^{19} 1·5538—1·5540. These were recombined and, on dilution with pentane, deposited solid 1 : 2-*dibromo*cyclo*decane* which sublimed at 100°/0·6 mm. and then had m. p. 121° (with a transition at 102°) (Found: C, 40·1; H, 6·3; Br, 53·0. $C_{10}H_{18}Br_2$ requires C, 40·3; H, 6·1; Br, 53·6%). Attempted dehydrobromination of the dibromide by the method of Kohler *et al.*[10] gave non-homogeneous products.

Attempts to convert *cis*-*cyclo*decane-1 : 2-diol (m. p. 139°, prepared by reduction of sebacoin with W7 Raney-Nickel in ethanol) into dibromo*cyclo*decane by treatment with hydrogen bromide in acetic acid at room temperature gave 1-acetoxy-2-bromo*cyclo*decane, b. p. 96°/0·2 mm., n_D^{24} 1·5059 (Found: Br, 29·6. Calc. for $C_{12}H_{21}O_2Br$: Br, 28·9%) (Blomquist *et al.*,[4] give b. p. 112—116°/0·6 mm., n_D^{20} 1·5098), while similar treatment of *trans*-*cyclo*decane-1 : 2-diol (m. p. 50°) gave unchanged material. Reaction of the *cis*-diol with phosphorus tribromide in chloroform gave non-homogeneous products.

1-*Bromo*cyclo*decene*.—Sebacoin (100 g.), copper acetate (220 g.), acetic acid (600 ml.), and water (600 ml.) were heated under reflux for 2 hr. The solution was diluted with water (3 l.) and extracted with ether (3 × 600 ml.). The ether extract was washed with aqueous sodium hydrogen carbonate and filtered. The precipitate (5 g.) was 2 : 5-dihydroxy-2 : 6-3 : 5-bisheptamethylene*cyclo*hexane-1 : 4-dione [11] which after sublimation in a high vacuum and recrystallisation from toluene had m. p. 255° (Found: C, 71·5; H, 9·9%; *M*, in camphor, 319. Calc. for $C_{20}H_{32}O_4$: C, 71·5; H, 9·55%; *M*, 336). Distillation of the ether layer gave *cyclo*decane-1 : 2-dione (80·8 g., 82%), b. p. 104—110°/12 mm., which crystallised from *n*-pentane and then had m. p. 41°, $\lambda_{max.}$ 2700, 2800, and 3950 Å (ε 27, 27, and 15, respectively) in EtOH (Prelog *et al.*[3] give m. p. 40°).

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[10] Kohler, Tishler, Potter, and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 1057.
[11] Raphael and Scott, *J.*, 1952, 4566.

The dione (53 g.) in ethanol (250 ml.) was treated with 95% hydrazine hydrate (40 g.), giving the bishydrazone, m. p. 108—110°, unchanged after repeated recrystallisation from ethanol [Prelog *et al.*[3] give m. p. 126—130° (decomp.); the discrepancy may be due to differences in rate of heating].

The bishydrazone (9·5 g.) was added in six portions during 30 min. to a vigorously stirred mixture of mercuric oxide (23 g.), powdered potassium hydroxide (1 g.), anhydrous sodium sulphate (20 g.), and dry toluene (100 ml.) heated under gentle reflux. After a further 2 hr., the mixture was cooled and filtered, and the solution was passed through a column of alumina (10 g.; Grade II [12]). Fractionation gave *cyclo*decyne (4·6 g.), b. p. 94°/26 mm., n_D^{20} 1·4910; Blomquist *et al.*[4] give b. p. 203—204°/740 mm., n_D^{20} 1·4950.

Hydrogen bromide, generated by slowly adding hydrobromic acid (48%, 7·5 ml.) to excess of sulphuric acid, was passed into *cyclo*decyne (4·0 g.) during 1·5 hr. Distillation gave slightly impure bromo*cyclo*decene (6·3 g.), b. p. 80—82°/1 mm., n_D^{20} 1·5230 (Found: C, 56·1; H, 8·1; Br, 35·8. Calc. for $C_{10}H_{17}Br$: C, 55·6; H, 7·9; Br, 37·0. Calc. for 1-bromo*cyclo*decene 97·5% + *cyclo*decyne 2·5%: C, 56·1; H, 8·0; Br, 35·8%).

cyclo*Dec-*1*-enecarboxylic Acid.*—1-Bromo*cyclo*decene (3·0 g.) was added to a stirred suspension of finely cut lithium (195 mg.) in ether (50 ml.) under nitrogen. After 5 min., the mixture became turbid and heat was evolved. After 4 hr., unchanged lithium (40 mg.) was filtered off through fine wire-gauze and the solution was added to powdered solid carbon dioxide (150 g.). Next day, 2N-hydrochloric acid (20 ml.) was added, and the ether layer was separated and extracted with aqueous sodium carbonate. The aqueous extract was acidified with concentrated hydrochloric acid, and the precipitate was extracted with ether. The ether extract was transferred to a vacuum retort; heating at 90—100°/10^{-4} mm. gave a sublimate (133 mg., 5%), m. p. 70—114° (Found: C, 72·6; H, 9·9. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·95%). Crystallisation from aqueous methanol gave cis(?)-cyclo*dec-*1*-enecarboxylic acid*, m. p. 130—131°, $\lambda_{max.}$ 2230 Å (ε 8600) in EtOH, $\nu_{max.}$ 2800 (s) (C–H stretching), 2600 (s) (O–H stretching), 1660 (s) (C=O stretching), 1625 (s) (C=C stretching), 1440 (s) ($\geq$C–H bending), 1365 (m), 1260 (w), 1150 (w), 926 (s) (O–H bending), 886 (m), and 720 (m) cm.$^{-1}$ (Found: C, 72·6; H, 9·9%).

The acid (40·4 mg.) was hydrogenated in acetic acid (2 ml.) in the presence of platinic oxide. Uptake of hydrogen ceased when 4·6 ml. at 20°/760 mm. (Calc., 5·1 ml.) had been absorbed. The catalyst was removed by centrifuging, and the acetic acid was distilled off at 10 mm. The residue was distilled at 10^{-5} mm., giving an oil which solidified and after crystallisation from *n*-pentane had m. p. 53·5—55°. The mixed m. p. with an authentic sample of *cyclo*decanecarboxylic acid [5] (m. p. 52—53°) kindly supplied by Professor V. Prelog (E.T.H., Zürich) was 52·5—55°.

Attempted Alkenylation of Benzaldehyde.—Benzaldehyde (1·3 g.) in ether (10 ml.) was added dropwise to a stirred solution of lithium alkenyl (from 1-bromo*cyclo*decene, 2·6 g.) in ether (85 ml.) under nitrogen. After 1 hr. at room temperature, saturated ammonium chloride (20 ml.) was added, the ether layer was separated and dried (Na_2SO_4–K_2CO_3), and the solvent removed. The residue was distilled at 100—120°/10^{-3} mm., giving: (i) a *product* [*di*(cyclo*decenyl*)?] (0·6 g.), n_D^{23} 1·5255, $E_{1\,cm}^{1\%}$ <5 between 2100 and 4000 Å (Found: C, 86·5; H, 12·3. $C_{20}H_{34}$ requires C, 87·5; H, 12·5%), which did not undergo hydrogenation (AcOH–PtO_2), but rapidly decolorised bromine water; (ii) a *product* (0·3 g.), b. p. 130—140°/10^{-3} mm., n_D^{23} 1·5655, $\lambda_{max.}$ 2280, 2510, and 2800 Å (ε 4400, 3900, and 6100, respectively) in EtOH, unchanged on addition of hydrochloric acid (Found: C, 83·6; H, 9·5. $C_{17}H_{24}O$ requires C, 83·6; H, 9·9%). Similar results were obtained on carrying out the metallation at −10°.

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[12] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.